

much attention to this question and who is now conducting a research for the Advisory Council of Scientific and Industrial Research; Dr. H. G. Colman, Chairman of the Joint Refractory Materials Committee of the Institution of Gas Engineers and the Society of British Gas Industries; Major F. J. Bywater, now on active service, who was formerly Chairman of the above-mentioned Committee, is the author of the excellent paper on "Refractory Material" read before the Institution of Gas Engineers, referred to later on in these remarks; Mr. F. W. Harbord, who is also engaged in conducting inquiries and researches with regard to refractories in connection with another Special Committee; Professor W. A. Bone, the Chairman of the Fuel and Refractories Committee of the British Association.

Professor W. G. Fearnside, of the Sheffield University, has paid special attention to this subject; Dr. B. G. H. Boswell, who will speak to-night on refractory sands; Dr. A. Strahan, the able Director, and Mr. J. Allen Howe, of the Geological Survey and Museum, are present with us this evening and have been good enough not only to prepare some interesting information, but also exhibits; Mr. Ezer Griffiths, M.Sc., who has done excellent research work for the National Physical Laboratory in this direction; Messrs. Cliff, Page, Searle, and several others who will contribute to the discussion to-night from the point of view of the manufacturers; also many others.

The Chief Refractories.—The following probably represents the chief refractories:—

- (a) Silica.
- (b) China clay.
- (c) Magnesite.
- (d) Dolomite.
- (e) Chromite.
- (f) Bauxite.
- (g) Graphite.
- (h) Zirconite.

There have been considerable importations into our country from abroad of refractories, when without doubt in most cases equally as good, if not better, material has been in our own country at our very door. Moreover, this subject not only interests the ferrous and non-ferrous metallurgist, but also the makers of the various pottery, porcelain, and other similar wares. As an example, my own firm can plead guilty to having purchased material from abroad when it was at home and near at hand; I believe there are many others who would have to admit the same impeachment.

We have, therefore, specially to thank Dr. Strahan, Mr. J. Allen Howe, and Dr. Lamplough, of the Geological Survey and Museum, Jermyn Street, who have quite recently taken up the subject most vigorously and shown that at home in our own kingdom we possess much more valuable stocks of raw products to be used for the purpose of refractories than has been ordinarily imagined.

Professor W. R. Dunstan, F.R.S., of the Imperial Institute, has also given attention to this subject and has sent exhibits for this evening's proceedings.

Ganister.—The great importance of obtaining a good refractory is shown by the fact that the first development on a large scale of the Bessemer process in Sheffield was chiefly because there happened to be in that city a particularly fine quality of material known as "ganister." Sir Henry Bessemer could not find material suitable for lining his converters, in which

there is a combination of not only high temperature but slagging and erosive action. Sheffield ganister was found to meet this condition better than any other material, thus enabling Bessemer to carry his process into practical working success.

The following is a typical analysis of ganister :—

Silica	95	per cent.
Alumina	2	"
Iron oxide	0.5	"
Lime	1.00	"
Magnesia	0.6	"
Water	1.75	"

This material has been used for several generations to line the furnaces, known as "pot holes," in which Sheffield crucible steel is made, and it is still unsurpassed for this purpose.

Standard Specifications.—The pamphlet on *Standard Specifications for Refractory Materials*, published by the Institution of Gas Engineers in 1912, is of special interest in connection with the important subject being considered this evening, and it is being reprinted (by kind permission) as an Appendix to the present symposium. (See p. 180.)

Mr. Bywater's Paper.—An important paper was also read about the same time before the Institution of Gas Engineers by Mr. Frederick J. Bywater on the question of refractory materials. This paper is one of the most valuable contributions on the subject which the writer has seen, and by the kindness of the Institution of Gas Engineers this paper is being reprinted as a fitting Introduction to the present collection of Papers. (See p. 32.)

Method of Testing Bricks.—In one of the American papers reference is made to a simple but fairly effective method, shown by the following figure (Fig. 1), of testing refractory bricks, which has been brought forward by the Armstrong Cork and Insulation Company, of Pittsburg, Pa. Their experiment is carried out by playing the hottest flame obtainable, Bunsen burner or other gas jet, against the face of the brick to be tested. The surface naturally becomes white hot, but if the brick is not of the highest quality it will conduct the heat too quickly and soon become too hot to be held. This experiment could easily be carried out upon a brick of special qualities and a firebrick or common red brick, so that comparison is readily obtained.

The maker claims that he produces these bricks chiefly from diatomaceous earth (in whose fronds are secreted very large quantities of silica), which he states is one of the best non-conductors of heat known. The exact nature of this earth is not mentioned, but no doubt before long it will be possible to obtain supplies in this country, so that tests can be carried out.

It is claimed for this Nonpareil insulating brick that its insulating efficiency is ten times that of either common or firebrick, also that one $4\frac{1}{2}$ -in. course installed in the walls, arches, and bottoms of furnaces, ovens, boiler settings, hot-blast mains, and kindred high temperature equipment, will reduce the loss of heat as much as would 45 in. of ordinary brick. This is a strong statement, but the firm seems willing to prove that it is correct.

Dr. Percy.—It should be borne in mind that it was in Jermyn Street, where Dr. Strahan is now the Director, that Dr. Percy, to whom all of us still owe so much in our metallurgical education and training, laboured for so many years at the Royal School of Mines. In Dr. Percy's justly renowned work on metallurgy, when speaking of that portion relating to refractory materials, he said, "We must give the devil his due that we are probably indebted to the Germans to a greater extent than is commonly supposed for

the development of our mineral resources, since the introduction of German miners and metallurgists into England about three centuries ago, through the wisdom of Elizabeth."

In his work he only devotes a small space to refractory materials, including portion of a chapter on fire-clays. In this is given the following analysis, made in 1860, of the famous Dinas bricks:—

Silica	97 to 98½ per cent.
Alumina	0·75 to 1·50 "
Protoxide of iron	0·20 to 0·50 "
Lime...	0·20 "

Past Information on Refractories.—As an example of the scarcity of information, I have looked over some of the principal works on metallurgy and find that but little space or attention has been given to it.

Kohn in his book *Iron and Steel Manufacture* (1868) has an excellent chapter on "Moulding Sands," and there deals with refractories. He gives the following brief but on the whole accurate interpretation, which is the more remarkable seeing it was nearly fifty years ago, of the parts played by the different constituents of refractories.

The higher the proportion of silica the more refractory the substance, but its cohesion is then lessened, it is difficult to form it into a compact body, the moulds crack in drying and are liable to be destroyed by currents of metal running into them.

Alumina and magnesia are the substances which render the mass cohesive and plastic; but the excess of the former substance lessens the refractory qualities of the mould, it being subject to vitrification at a high temperature. Magnesia is highly refractory, and forms an excellent cement for silicious sand, but its quantity is limited by the necessity of keeping the whole mass porous for the escape of gases from the liquid metal.

The presence of metallic oxides in the sand always impairs its refractory qualities; still more undesirable is the presence of lime. Lime, if present as carbonate, will give off its carbonic acid at a high temperature, causing bubbles; if present as silicate or caustic lime, it will vitrify in contact with the sand. Similar results are produced by the metallic oxides.

He also describes, with great solemnity, how an important fire-clay mixture was brought over to this country from Bochum, called Riepe's mixture, by the Sheffield firm then known as Naylor, Vickers & Son, the working of which was a great secret.

Professor Howe, in his great work on *The Metallurgy of Iron*, gives some useful information, but only with regard to refractories such as used in the Bessemer process; that is, he deals chiefly with refractories in their bearing upon linings for Bessemer converters.

Professor Bradley Stoughton, in his *Metallurgy of Iron and Steel*, beyond two or three pages of general references, says very little.

Sir William Roberts-Austen, in his *Introduction to the Study of Metallurgy*, gives a few useful pages on general questions relating to refractories, but nothing of a very definite nature.

Refractories for Furnace Linings.—There are three classes of refractory materials now used—

- (a) Acid ... Dinas rock, ganister, fire-clays.
- (b) Basic ... Dolomite, magnesite.
- (c) Neutral ... Bauxite, chrome, iron ore, graphite, and a few fire-clays.

On satisfactory acid linings depend the acid steel process, such as the acid, Bessemer, and acid open hearth.

On satisfactory basic linings the success of the basic steel process practically depends, as in the presence of acid linings the necessary dephosphorization cannot take place, any phosphorus oxide formed being converted and again deposited in the bath.

Neutral linings, whilst possessing certain advantages, are usually very expensive and cannot be easily applied. On the other hand, in electric furnaces acid linings can be used if desired; nevertheless, basic, neutral, and zirconia linings are found to give much better results, hence the importance of a study of their application to this special purpose.

For crucible work there is still only the choice of two materials; the ordinary Sheffield clay crucible made of what is called pot clay, which is a mixture of fire-clay, china clay, a little carbon, and sometimes small quantities of other special materials. The usual mixture is two-thirds raw and one-third burnt clay.

Plumbago crucibles are produced in large quantities, being composed of fire-clay and graphite suitably mixed. The objection to the use of these crucibles is that naturally in melting steel considerable carbonization often takes place, and material cannot be obtained of the same uniformity as that melted in the ordinary type of Sheffield crucible, which has been used ever since the time of Huntsman. It is an open secret that this is the reason for the uniformity of what is known as Sheffield crucible steel, which steel retains its position in the markets of the world.

Large quantities of millstone grit are found in the moor districts near Sheffield. Howe points out that in some cases blocks of millstone grit have been used with fair results.

With reference to bauxite, Professor H. Le Chatelier in a recent letter to the writer states that he considers this material of great importance. He points out that his father studied this matter very closely as far back as 1870, but found that the excessive porosity of this material and its contraction militated against its successful use in the form of bricks. He attributes the difficulty to the bauxite not being sufficiently calcined, and therefore the subsequent shrinkage was not avoided. With the better means now available this can be done; a great improvement in practice should therefore result.

Professor Le Chatelier regards the bauxite bricks to have a much higher melting-point than those made from the very best silica.

This matter would appear to be well worth following up in this country. Messrs. J. H. Sankey & Son, Essex Wharf, Canning Town, London, E., are at the present time giving special attention to the subject.

Zirconia.—In addition to the ordinary and well-known refractories in which silica and alumina play the chief parts, the somewhat rare product zirconia has recently received much consideration. In the interesting book published not long ago on *The Rare Earths*, by Mr. S. I. Levy, B.A., B.Sc., a chapter is devoted to the study of zirconium and its oxides. In this reference is made to the importance of its use as a refractory. This oxide was isolated as a new earth from zircon, obtained from Ceylon by Klaproth in 1789. A little later the new earth was obtained also from hyacinth. The new oxide was examined in 1818 by Berzelius, who found it resemble alumina. The formula Zr_2O_3 was then given.

Whilst zirconium is fairly widely distributed in nature, it is in very small quantities, and can be rightly classed as one of the rarer elements. The most important source of the element was until quite recently the mineral zircon with its gem-varieties, hyacinth and jargon.

The chief source of the ore at present is the naturally occurring oxide, baddeleyite, which is almost pure zirconia ($ZrO_2 = 96.5$ per cent.). This was

discovered in 1892, particulars of which are given by Fletcher in the *Mining Magazine* of 1893. This has been obtained from the pyroxenite sand of São Paulo, South Brazil, also in Ceylon and in Montana, U.S.A. Its melting-point is probably about $2,700^{\circ}\text{C}$., and at $3,000^{\circ}\text{C}$. it begins to volatilize.

Zirconia occurs in crystalline rocks, specially in granular limestone, schist, gneiss, syenite, and granite. The most frequent forms are the silicates of zirconium, ZrSiO_4 .

The chief localities are in alluvial sands in Ceylon, the Urals, in the gold districts of Australia, Brazil, and in many places in North America.

The late Dr. Sorby, F.R.S., of Sheffield, noticed in this mineral a peculiar absorption spectrum, and he first thought that it contained a new element, to which he gave the name of jargonium. It was, however, subsequently found that these spectrum lines were caused by the presence of uranium oxide.

It has been shown by Rieke in *Sprechsaal*, 1908, No. 41, that whilst the oxide is very suitable for the manufacture of highly resistant crucibles and other refractories, its use is restricted by the fact that it is somewhat easily reduced by carbon at high temperatures, forming the carbide.

It appears that as early as 1904 the use of zirconia was suggested for cutting muffles, retorts, and tubes which are required to withstand high temperatures. This was given in the German patent: Pyfahl, No. 156,756. In 1906 it was proposed by the Heræus Company, in their German patent, for the manufacture of crucibles in which rock-crystal (quartz) was fused for the preparation of quartz-glass, since zirconia is not attacked by molten silica. It promises to be of the greatest use in all cases where a very refractory material, stable towards the ordinary chemical reagents, is required.

Metallic zirconium has also been obtained by the calcium reduction process, introduced by Kuzel and Wedekind. Whilst zirconia is not reduced by powdered aluminium (Goldschmidt's process), alloys of zirconium and iron can be easily obtained by reduction of the mixtures of the two oxides by this method. It appears alloys containing up to 35 per cent. of zirconium can be obtained; this ferro-zircon, as it is called, has been to some extent recently replaced by ferro-titanium for the purification of steels. Several German patents have been taken out for this purpose.

It is also stated that any addition of small quantities of zirconium to steels (brass, copper, etc.) is said to secure sound castings, whilst increasing considerably the strength and resistance to acids of the metal.

For most of the above information the writer is indebted to Mr. S. I. Levy in his very excellent work entitled *The Rare Earths*.

Another very interesting article on the subject is that by Mr. H. Conrad Meyer, "Further Notes on the Refractory Properties of Zirconia," which appeared in the *Metallurgical and Chemical Engineering* of April 1915. Much useful information is there contained regarding heat tests, fire shrinkage, selection of binders, fire-clay bonds, and zirconia crucibles and similar shapes.

An analysis of zirconia was given in a previous paper in December 1914 by the same author, which was as follows:—

ZrO_2	84.10
SiO_2	7.74
Fe_2O_3	3.10
TiO_2	1.21
Al_2O_366
Loss on ignition...	2.72

The Foote Mineral Company of Philadelphia have paid a good deal of attention to this product. Zirconia, they say, owing to its high degree of infusibility, high resistance to basic or acid slags, low thermal conductivity, low coefficient of expansion, can be employed at the highest temperatures without the destruction of the furnace linings. The material is supplied as zirconium oxide, also in the form of cement affording a plastic bond when wet.

Much useful information with regard to zircon, zirconia, and zirconite, as it is often indiscriminately termed, is found in Dana's book *Minerals and How to Study Them* (1902), also in Mendeléeff's *Principles of Chemistry* (1905). Incidentally the latter points out that zirconium compounds are generally prepared from powdered zircon by fusing it with sodium carbonate and then boiling in water. An insoluble white residue is obtained consisting of a compound of the oxides of sodium and zirconium, which is then treated with hydrochloric acid and the solution evaporated to dryness. The silica is thus converted into an insoluble form, and zirconium chloride obtained in solution. Ammonia precipitates zirconium hydroxide from this solution as a white gelatinous precipitate, $\text{ZrO}(\text{OH})_2$. When ignited, this hydroxide loses water, and in so doing undergoes spontaneous recalcination and leaves a white infusible and exceedingly hard mass of zirconium oxide, ZrO_2 , having a specific gravity of 5.4 (in the electric furnace, ZrO_2 fuses and volatilizes like SiO_2 —Moissan). Owing to its infusibility, zirconium oxide is used as a substitute for lime and magnesia in the Drummond light.

In Sterry Hunt's excellent works, *Systematic Mineralogy* (1891) and *Mineral Physiology and Physiography* (1891), some useful information is also given.

Bibliography.—With reference to the bibliography, it will be seen that information in this form is quite scanty. In view, therefore, of the importance of the subject, I have prepared from my own series of references, extending over a period of some thirty years, and taken from the technical and scientific press, the various papers shown in the accompanying Tables I and II, the former comprising books on the subject, and the latter references in the technical press. Should any member of the Society like to refer to any particular book or extract referred to in these tables, they are with pleasure at his service.

The divisions of these press references, covering pamphlets, papers, and cuttings, are in the following order—

- (a) Firebricks and clay products.
- (b) Silica products.
- (c) Magnesite products.
- (d) Chromite products.
- (e) Bauxite products.
- (f) Zirconia.
- (g) Graphite.
- (h) Comparative tests.
- (i) Miscellaneous.

There are in all 197 papers, of which 64 are British, 14 French, 67 American, and 46 German.

EXHIBITS.

In addition to the excellent and complete set of exhibits from various members of our Society, also other friends and firms, it has occurred to me that in these introductory remarks to the symposium of Papers now presented

it would be well to exhibit specimens of refractory materials, also those which are definitely known to have given good and bad results, with a view to obtain some discussion with regard to reasons for the respective satisfactory and unsatisfactory behaviours. Table III gives a full description of these, from which it will be seen that analysis only does not by any means tell us all we want to know. Evidently there are physical conditions prevailing in these refractories which we do not yet understand, just as in bars of the same steel and composition one may obtain good and bad tensile and elongation qualities, the causes of which we are, however, now fairly well able to detect. Whilst, therefore, it is not analysis alone which will tell us why one refractory is good and another bad, we have to look for the physical conditions of the respective combinations of the elements present, that is, apart from their chemical constituents.

I therefore add the following information which has come to me from my company's laboratories in Sheffield. I give these fully because they represent the practical views of those handling daily various types and qualities of refractories.

Sand for Open Hearth Bottoms, of which both British and Belgian specimens are submitted.

Whilst Belgian sand for open hearth furnace bottoms was in universal use before the war, when these supplies were stopped it was necessary to experiment with British sands. This was at first done by mixture with Belgian material, but ultimately a British sand has been found to give practically the same results as the foreign product since its properties were correctly understood.

In this respect I would suggest that those in difficulty and doubt would often be able to obtain most interesting and valuable information from Dr. Strahan, the Director of the Geological Survey and Museum in Jermyn Street.

Silica Bricks.—One of the chief difficulties experienced with silica bricks is insufficient burning, known to furnace men as "half-bakes." Such bricks flux almost as readily as firebricks. If such bricks are not detected before putting in the furnace, it may mean shutting down the furnace for repairs, although the rest of the furnace is quite good.

Fire-clay Stoppers.—Stoppers are quite as important as nozzles. Magnesite does not appear to make a successful stopper as hitherto manufactured, owing to its liability to crack and spelch. When using magnesite nozzles it frequently happens that the fire-clay stopper ends collapse during the casting, and fused pieces pass through the nozzles. Fire-clay nozzles wear badly as compared with magnesite, and usually the orifice is double the size after similar work, which means that a good deal of silica has entered into the steel and is the cause of subsequent trouble.

As regards the above experiments I am this evening submitting specimens of—

(a) A bad fire-clay stopper and the slag produced after passing through the nozzle.

(b) Fire-clay nozzle for comparison with a good magnesite nozzle (see next paragraph). Both these have done the same work.

Magnesite Nozzles, of which both good and bad specimens are submitted.

Fig. 2 shows magnesite nozzle before and after use. No less than 77 separate pourings were made with this nozzle from a ladle containing 28 tons of open-hearth carbon steel. It will be seen that the pouring hole in the nozzle had a diameter of 1 in. before use; after 28 tons of steel had run through this the diameter still remained 1 in.

As a comparison, Fig. 3 gives the results obtained with an ordinary fire-clay nozzle. With this 77 pourings were made from a ladle containing 28 tons of open-hearth steel. It will be seen that the diameter of this ordinary fire-clay nozzle was increased to no less than 2 in. It is therefore quite clear how intermingled slag is found in steel; the silica and alumina is slagged off and is carried into the steel ingot or casting being poured, some of it floating to the top, but in some cases it remains on the side of the ingot, or even embedded in the steel.

In Fig. 4 an ordinary fire-clay stopper is shown before and after use.

Magnesite nozzles have given excellent results when used for a large number of castings from one heat, also with steels containing 0.90 per cent. of manganese and upwards. This is due to the fact that such steels have a severe chemical action on the fire-clay nozzles. The use of magnesite for nozzles is not a new idea, but owing to the more stringent specifications in the manufacture of steel this use of magnesite is now being brought forward. One of our nozzle experiments was made with a combination of magnesite and fire-clay, but this was not successful, as the acid flux from the fire-clay attacked the magnesite and caused too much increase in the size of the orifice in the nozzle. It is also extremely important that these nozzles should be perfectly dry. The bad sample exhibited is an example of a nozzle delivered wet, which gave way in the middle of casting a 25-ton heat.

Plumbago Stoppers and Nozzles, specimens of each of which are submitted.

A number of these have been tested, and the results obtained so far have been no better than those with fire-clay.

Magnesite Bricks.—As is well known, this country was unfortunately, partly through ignorance and lack of enterprise, to some extent dependent upon Austrian magnesite. Supplies have also been obtained from Grecian mines.

Dolomite Bricks.—For use on the walls and roofs of electric furnaces, these would be invaluable if means could be devised to prevent perishing.

Zirconia.—Experiments are now in progress with this material, with regard to the practical application of which it will no doubt be possible to submit fuller information later on.

ANALYSES.

In addition to the above I have also prepared from our laboratory records a large number of analyses of British and foreign refractories, which are shown in Tables IV, V, VI, VII, and VIII. From these it will be seen that they come from "all the ends of the earth"; not only British, but Belgian, French, German, and American. In view of the scanty nature and little work which has been done in this direction, I trust this information will be found of interest to those within the Empire who are interested in this important subject.

I have had prepared a few photomicrographs, shown in Figs. 5-13, as an illustration of the use of microscopy in the study of refractories. A good deal of attention has been paid to this side of the subject in America, where useful papers have been read before the American Foundrymen's Association with regard to such examination of refractory materials on sands of various kinds.

The following is only put forward in a tentative way and with a view to arouse interest on this particular side of the research with regard to refractories. Professor Fearnside, of the Sheffield University, is also dealing with this subject in his excellent paper on the "Application of Petrographic Methods to the Study of Refractory Materials."

Whilst it has been stated that analysis is not by itself sufficient guide, it may be that the methods of determining the chemical composition of refractories have not been altogether perfect, and that in this respect there is room for improvement. On the other hand, it must still be borne in mind that, as in the case of iron, steel, and other products, analysis is the basis and basic principle of our knowledge of such materials.

Table IX gives the description of the sands of which I submit photomicrographs, together with the remarks upon these.

It should be mentioned that the sands from which the photomicros shown in Figs. 6, 11, 12, and 13 were prepared were washed with hot dilute HCl. This is to clear the grains from colouring matter, so that they stand out sharply in the photomicros in order that their size and varying capacity can be clearly seen.

Conclusion.—This subject of refractories has been treated in the past far too much in an empirical manner. Whilst in this country much has been done from the time of Wedgwood and others, yet let us now show the world that we intend to lead the way, and take up this important branch of metallurgy in a proper scientific manner. Much research is required in addition to that carried on at the works of the manufacturers. Research centres such as the National Physical Laboratory, the Metallurgical Section of the Sheffield University, and still more recently the Advisory Council for Scientific and Industrial Research, are all prepared to render help, either by carrying out actual researches or finding research grants to those they are satisfied will wisely spend such grants and make use of such information. It is to be hoped that this evening's symposium of Papers will result in extended knowledge on this important subject. If so, the Council of the Faraday Society will be well repaid for the trouble they have taken in its preparation.

In conclusion, I take this opportunity of thanking my assistants, Messrs. Dawson, Swift, Elliot, Main, Mortimer, and others, for their useful help in the preparation of this introductory address.

TABLE I.

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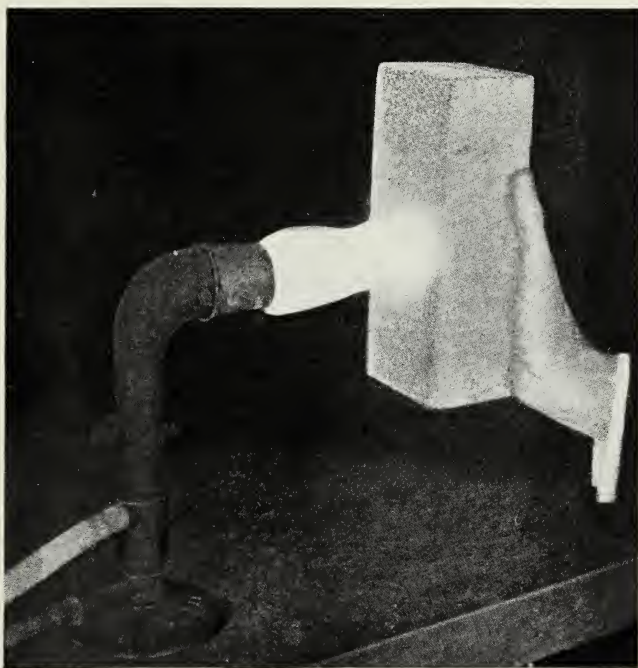


FIG 1.

This simple test will demonstrate the heat insulating quality of various types of firebricks.

MAGNESITE NOZZLE.



FIG. 2.—Before and After Use. No. of Castings made, 77. Total weight, 28 tons.

FIRE-CLAY NOZZLE.

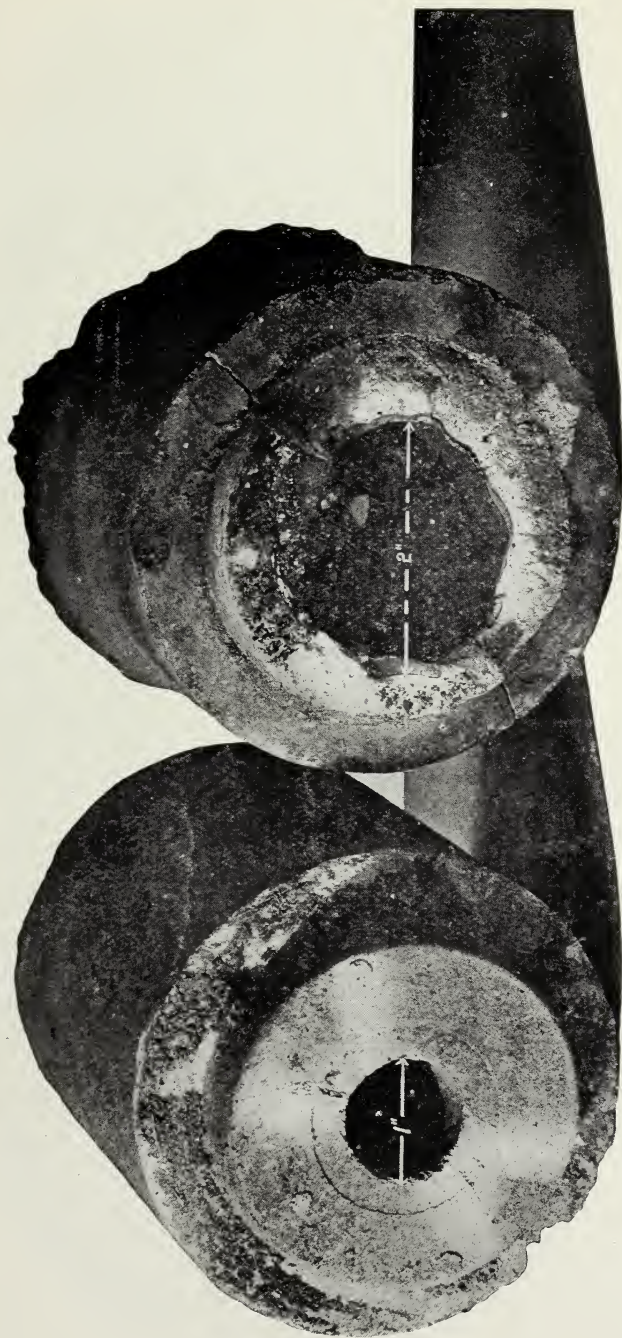


FIG. 3.—Before and After Use. No. of Castings made, 77. Total weight, 28 tons.

FIRE-CLAY STOPPER.



FIG. 4.—Before and After Use. No. of Castings made, 77. Total weight, 28 tons.

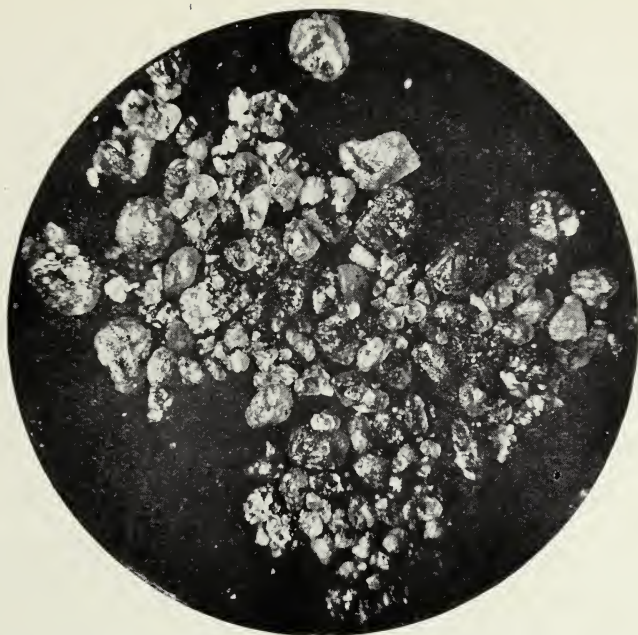


FIG. 5.—Workshop Yellow Sand (not treated with HCl). $\times 15$.

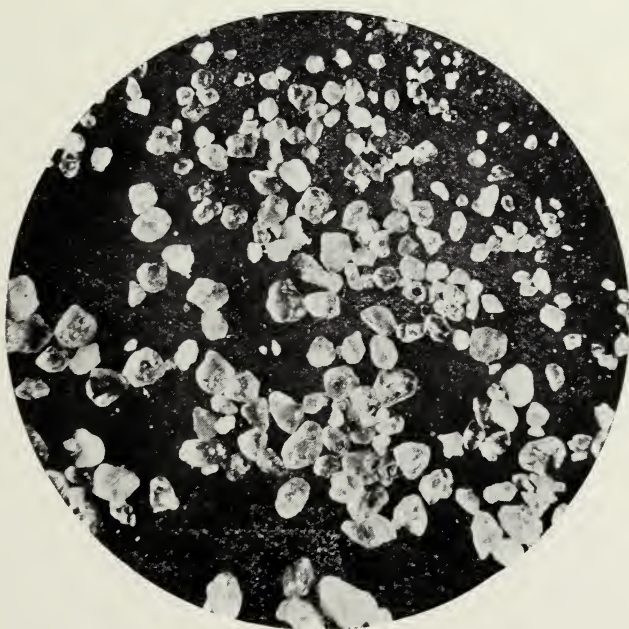


FIG. 6.—Workshop Yellow Sand (after treatment with HCl).

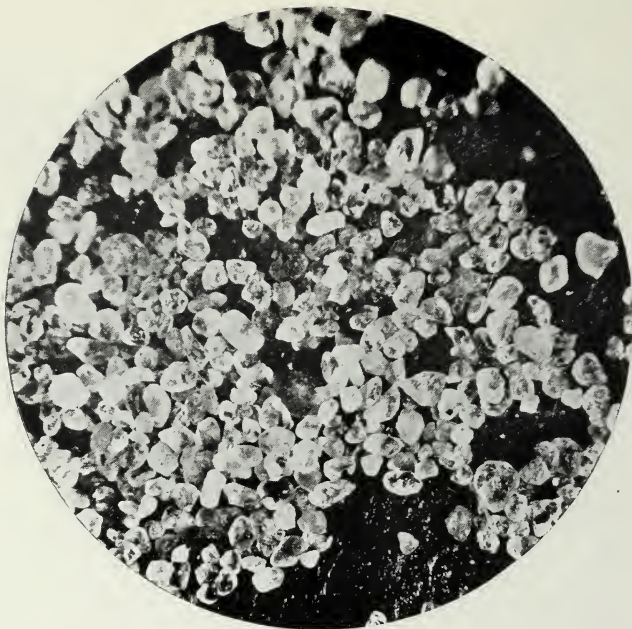


FIG. 7.—Dutch Silver Sand. $\times 15$.

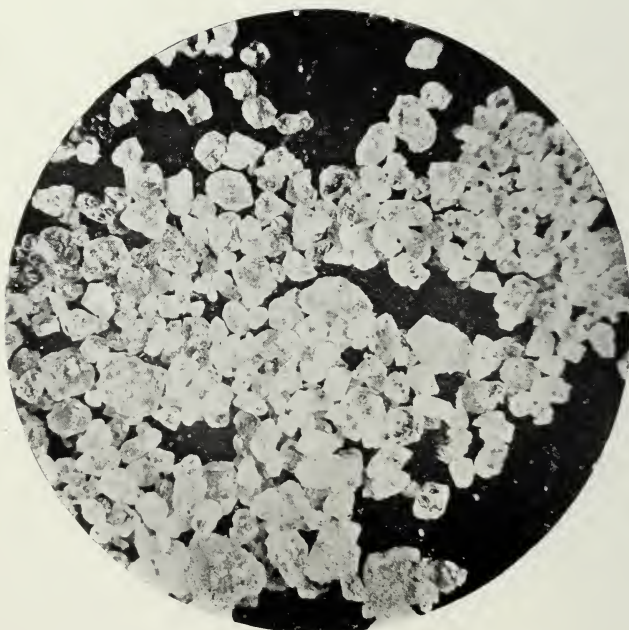


FIG. 8.—Scotch Silver Sand. $\times 15$.

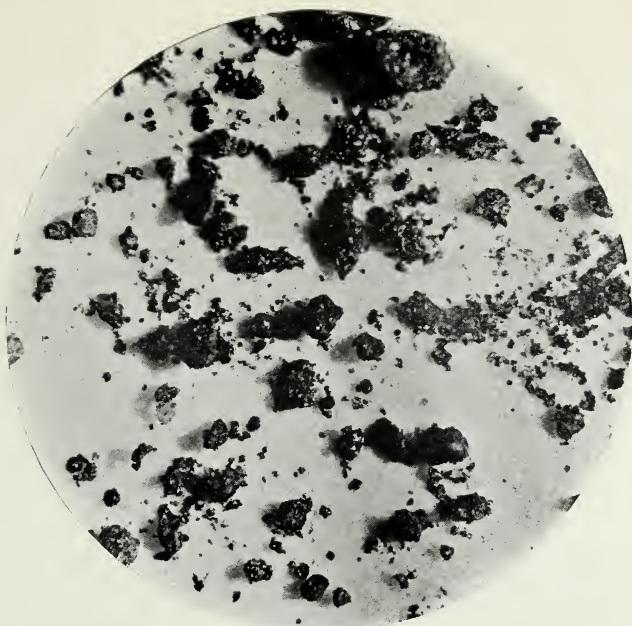


FIG. 9.—Back Facing Sand. $\times 30$.



FIG. 10.—Scotch Fire-clay. $\times 30$.



FIG. 11.—Workshop Red Sand. $\times 15$.



FIG. 12.—Leighton Buzzard Sand. $\times 15$.



FIG. 13.—French Red Sand. $\times 15$.

TABLE I (*continued*).

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1914. DOELTER, C. : Handbuch der Mineral Chemie, vol. ii.
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1915. LEVY, S. I. : The Rare Earths.
1915. KENWORTHY, J. : Clay, Firestone and Ganister in the Little Don Valley.
1916. KELLER, P. : Ueber die Fabrikation und Anwendung feuerfester. Clay and Pottery Industries, being collected Papers from the County Pottery Laboratory, Staffs.
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TABLE II.

	Date.	Title.	Author.	Publication.	Country.	Description.
		<i>A. Firebricks and Clay Products.</i>				
15	February	Refined Slag in Firebrick ...	Elbers, A. D.	Engineering & Mining Journal	United States	Cutting
22	February	Determination of Fireproof Qualities of Clay	Seger, Dr.	—	Germany	Pamphlet
—	February	Experiments for Determining the Refractoriness of Fire-clays	Hofman, H. O., and Desmond, C. D.	American Institute of Mining Engineers	United States	Pamphlet
—	March	Further Experiments for Determining the Fusibility of Fire-clays	Hofman, H. O.	Ibid.	United States	Pamphlet
—	—	Fuel and Refractory Materials ...	Sexton, A. H.	—	Great Britain	Pamphlet
—	September	Fire-clays ...	Hopkins, T. C.	Mines and Minerals Engineering & Mining Journal	United States	Cutting
24	September	Clay Resources of Alabama and the Industries Dependent on Them	Smith, A. E.	—	United States	Cutting
15	June	Variation Found in the Use of Firebricks	—	Stahl und Eisen	Germany	Cutting
22	October	Notes on the New Jersey Firebrick Industry	Ries, H.	Iron Age	United States	Cutting
—	—	Refractory Materials for Furnace Linings	Scott, E. K.	Transactions Faraday Society	Great Britain	Pamphlet
—	—	Refractories and the Like, Furnaces	Chatenet	Revue de Métallurgie	France	Cutting
—	—	Electric Heating and its Application to the Fusion and Firing of Refractory Materials	Hutton, R. S.	English Ceramic Society	Great Britain	Pamphlet

—	July	1905	Notes on Heat Insulation, particularly with regard to Materials used in Furnace Construction	Hutton, R. S., and Beard, J. R.	Transactions Faraday Society	Great Britain	Pamphlet
23	August	1906	Firebrick Problems in Metallurgy	Greaves-Walker, A. F.	Iron Trade Review	United States	Cutting
15	February	1908	The Valuation of Fire-clays ...	Page, E. P., and Rees, W. J.	Journ. Soc. Chem. Industry	Great Britain	Cutting
18	June	1908	Refractory Material ...	Bywater, F. J.	Institution of Gas Engineers	Great Britain	Pamphlet
31	November	1908	Heat Conductances through Walls of Furnaces	Hering, Carl	American Electro-chem. Society	United States	Pamphlet
—	May	1909	Conductivity, Porosity, and Permeability of Refractories	Wologdine, S.	—	France	Cutting
2	September	1909	Thermal Conductivity of Fire-clay at High Temperatures	Clement, J. K., and Egy, W. L.	University of Illinois Bulletin	United States	Pamphlet
26	September	1910	Changes in the Composition of Firebricks	Blasberg, Dr.	Iron and Coal Trades Review	Germany	Cutting
15	December	1911	Testing of Clay Refractories ...	Bleining, A. V., and Brown, G. H.	Bureau of Standards	United States	Pamphlet
—	—	1911	Causes of the Expansion of Dinas Brick	Holmquist	Tonindustrie Zeitung	Germany	Cutting
—	—	1911	The Refractory Qualities of Dinas Brick	Grum-Grzmailo	Stahl und Eisen	Germany	Cutting
—	—	1912	Melting-points of Firebricks	Kanolt, C. W.	Bureau of Standards	United States	Pamphlet
—	November	1912	Standard Specifications for Refractory Materials	—	Institution Gas Engineers	Great Britain	Pamphlet
—	February	1914	Relative Thermal Conductivity of Silica and Clay Brick	Marshall, S. M.	Met. and Chem. Eng.	United States	Cutting
5	March	1914	Tests for Firebrick and Clay	Mowat, J. F.	Iron Trade Review	United States	Cutting
19	March	1914	Testing of Refractories ...	Canaris, C.	Stahl und Eisen	Germany	Cutting
29	January	1915	Refractory Materials and the War	Searle, A. B.	Journal Royal Society of Arts	Great Britain	Extract
—	February	1915	An Examination of Firebricks	Patterson, W. H.	Met. and Chem. Eng.	United States	Cutting
22	April	1915	Thermal Conductivity of Refractories	Dudley, Jun., Boyd	American Electro-chem. Soc.	United States	Pamphlet

TABLE II (continued).

Date.	Title.	Author.	Publication.	Country.	Description.
<i>A. Firebricks and Clay Products (continued).</i>					
—	September	Seaver, K.	—	United States	Pamphlet
25	September	Dougill, G., Hods- man, H. J., & Cobb, J. W.	Society of Chemical Industry	Great Britain	Extract
—	November	Heisel, W. A.	Ohio Society of Engi- neers	United States	Pamphlet
8	January	Granger, A. (Chief of Testing Labora- tory, National Sevres Factory)	—	France	Pamphlet
20	January	Cobb, J. W.	Stahl und Eisen Coke Oven Managers' Assn., Leeds	Germany	Cutting Pamphlet
—	March	Quigley, W. T.	Met. and Chem. Eng. Iron and Coal Trades Review	Great Britain	Extract
15	June	West, J.	—	Great Britain	Cutting
16	June	Nesbitt, C. E., and Bell, M. L.	Iron Age	United States	Cutting
13	July	Mellor, J. W.	—	Great Britain	Cutting Pamphlet
—	No date	Mellor, J. W.	—	Great Britain	Cutting Pamphlet
—	No date	Mellor, J. W.	—	Great Britain	Cutting Pamphlet
—	No date	Mellor, J. W.	—	Great Britain	Pamphlet

B. Silica Products.

1897	The Behaviour of the Different Forms of Silicic Acid towards Caustic and Carbonated Alkaline Solutions	Langbe and Milberg	Zeit. für Angewandte Chemie	Germany	Cutting
1906	Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasilicate	Allen, White, and Wright	American Journal of Science	United States	Pamphlet
1906	Lime-Silica Series of Minerals ...	Day and Shepherd	Am. Journal of Science	United States	Pamphlet
1906	Melting Points of Silica or Quartz and other Refractory Materials	Lampen, A.	Journal of Am. Chemical Society	United States	Pamphlet
1906	Quartz Glass ...	Day and Shepherd	Science	Great Britain	Cutting
1907	Silica Brick Plant of the Robinson Clay Products Co., at Akron, Ohio	—	Iron Trade Review	United States	Cutting
1908	New Silica Brick Plant of the Harbison-Walker Refractories Co., at East Chicago, Ind.	—	Iron Trade Review	United States	Cutting
1910	Expansion and Thermal Hysteresis of Fused Silica	Kaye, G. W. C.	Philosophical Magazine	Great Britain	Pamphlet
1911	On the Behaviour of Fused Silica at High Temperatures	Blackie, A.	Transactions Faraday Soc.	Great Britain	Pamphlet
1911	Notes on the Manufacture of Silica Brick by the "Anaconda" Method	Greaves-Walker	Trans. Amer. Ceramic Society	United States	Pamphlet
1912	Fused Silica Ware, its Manufacture, Properties and Uses in the Chemical Industries	Marshall, A. E.	Metallurgical & Chemical Engineering	United States	Cutting
1912	Chemical Relations of the Various Modifications of SiO ₂	Schwarz, R.	Zeits. für Anorg. Chemie	Germany	Cutting
1912	The Constitution of Silica Brick ...	Endell, K.	Stahl und Eisen	Germany	Cutting
1912	Concerning Silica Brick for Open Hearth Furnaces	Lange, O.	Stahl und Eisen	Germany	Cutting
1913	The Stability Relations of the Silica Minerals	Fenner, Clarence N.	Am. Journal of Science	United States	Pamphlet
1913	The Transformations of Silica at Higher Temperatures	Rieke and Endell	Zeits. für Anorg. Chemie	Germany	Cutting

TABLE II (continued).

Date.	Title.	Author.	Publication.	Country.	Description.
<i>B. Silica Products (continued).</i>					
1913	Devitrification of Quartz Glass	...	Silikat Zeits.	Germany	Cutting
1913	La Silece	Rieke and Endell Chatelier, H. Le	Revue Univ. des Mines	France	Cutting
1913	Silica Quartzite	Endell, K.	Stahl und Eisen	Germany	Cutting
1913	Quartzite and Silica Brick...	Wernicke	Stahl und Eisen	Germany	Cutting
1913	Diatomaceous Earth	Bock, P. A.	Mineral Industry	United States	Cutting
1913	Glass Sand	Kümmel, H. B.	Mineral Industry	United States	Cutting
1913	Kieselguhr	—	Met. and Chem. Eng.	United States	Advert.
1914	Silicia Retorts	—	Refractory Mat. Com. of Institution of Gas Engineers	—	Report
1915	Diatom Heat-Insulating Brick	...	Met. and Chem. Eng.	United States	Cutting
1916	High Temperature Insulation	...	Journal Am. Soc. M.E.	United States	Extract
1916	Manufacture and Tests of Silica Brick for the By-Product Coke Oven	Boek, P. A. Seaver, Kenneth	Trans. Am. Inst. Min- ing Engineers	United States	Pamphlet
<i>C. Magnesite Products.</i>					
1890	Magnesite Lining for O.H. Fur- naces	—	Stahl und Eisen	Germany	Cutting
1890	Muller Basic Patent	Muller, A.	Iron Age	United States	Cutting
1890	Magnesite	Spaeter, C.	—	Germany	Pamphlet
1890	Lining of Basic Martin Furnaces with Magnesite	Lezius, H.	—	Germany	Pamphlet
1893	Importance of Magnesite for Basic Lining of Mild Steel Furnaces	Wedding, H.	Stahl und Eisen	Germany	Extract

—	—	1893	Magnesite Bricks for Martin Furnaces	Negris, P.	La Metallurgie	France	Extract
14	April	1893	Magnesia Firebricks	—	Engineering Journal of Society of Chemical Eng.	Great Britain	Cutting Extract
30	November	1893	Magnesite as a Refractory Material	—	Engineering and Mining Journal	United States	Cutting
11	July	1903	Magnesite: Its Uses and Value	Schnatterbeck, C. C.	Sydney Morning Herald	—	Cutting
21	October	1907	Interview with Mr. E. Kilburn Scott	—	Mineral Industry	United States	Cutting
—	—	1913	Magnesite	Judd, E. K.	—	—	Cutting
—	No date	—	Magnesite Lining in O.H. Furnaces	—	—	—	Cutting
—	September	1915	Magnesite	—	British Clayworker	Great Britain	Extract
—	—	1916	Magnesite Refractories	—	Revue de Metallurgie	France	Extract

D. *Chromite Products.*

—	No date	—	Chrome-iron Linings in O.H. Furnaces	Adelstjerna	—	Germany	Extract
6	No date	—	Chrome-ore Lining	Remaury	—	France	Extract
16	May	1889	Neutral Lining for Furnaces	Valton-Remaury	—	France	Pamphlet
—	November	1901	Chromite as Hearth Lining for Smelting Furnace	Glenn, W.	Engineering & Mining Journal	United States	Extract

E. *Bauxite Products.*

—	February	1894	Bauxite	Hayes and Laur	—	United States	Pamphlet
—	February	1906	Refractory Uses of Bauxite	Aubrey, A. J.	Electro-Chemical and Metallurgical Indus.	United States	Cutting
—	February	1916	Bauxite	—	Engineering	Great Britain	Extract
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Date.	Title.	Author.	Publication.	Country.	Description.
—	1915 Zirconia, a New Refractory	F. <i>Zirconia Products</i> . Meyer, H. C.	Journal of Institute of Metallurgy	United States	Extract
—	1915 Further Notes on the Refractory Properties of Zirconia	Meyer, H. C.	Met. and Chem. Eng.	United States	Cutting
5	October 1916 Zirconium as a Refractory	Richards, J. W.	Iron Age	United States	Cutting
No date	Lining Furnaces with Plumbago Paste	G <i>Graphite</i> . —	—	United States	Cutting
—	1907 Graphite, its Properties, Occurrence, Refining and Uses	Cirkel, F.	Ottawa Dept. of Mines	Canada	Pamphlet
22	April 1915 Temperature of Reaction between Acheson Graphite and Magnesia	Kowaler, O. L., and Grenfell, D. S.	—	United States	Pamphlet
23	January 1902 Refractory Materials	H. <i>Comparative Tests</i> . Longmuir, P.	Iron Trade Review	United States	Cutting
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21	February 1908 Refractory Materials	Holgate, T.	Engineering	Great Britain	Cutting
17	June 1910 Refractory Materials	Stansbie, J. H.	Iron and Coal Trades Review	Great Britain	Cutting
4	June 1914 Destruction of Refractories in Service	Rigg, G.	Stahl und Eisen	United States	Cutting
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—	1915 Behaviour of Refractories under Load	Mellor, J. W.	Ref. Mat. Com.	Great Britain	Report
—	1916 Prosecution of Research	—	Ref. Mat. Com.	Great Britain	Report

I. *Miscellaneous.*

		Solubility of Quartz in Alkaline Solutions	Rammelsberg	Annalen der Physik und Chemie, Poggendorf	Germany	Cutting
1861	—	On Kaolinite and Pholerite	—	Am. Journal of Science	United States	Pamphlet
1867	—	Pyrometrische Beleuchtung	—	Tonindustrie Zeitung	Germany	Cutting
1877	—	Use of Magno-chromite	—	—	Great Britain	Pamphlet
1894	January	Fusibility of Bottom Sand	Ferry, Chas.	Iron Age	United States	Cutting
1895	December	Volcanic Cement	Piron, H. J.	—	Germany	Pamphlet
1896	July	Properties of Quartzite	Cramer	Tonindustrie Zeitung	Germany	Cutting
1901	—	Mica: Its Occurrence, Exploitation and Uses	Cirkel, F.	Ottawa Dept. of Mines	Canada	Pamphlet
1905	—	Asbestos: Its Occurrence, Exploitation and Uses	Cirkel, F.	Ottawa Dept. of Mines	Canada	Pamphlet
1906	—	Action of Heat on Refractory Materials	Mellor, J. W., and Austen, F. J.	Trans. Engl. Ceramic Soc.	Great Britain	Pamphlet
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1909	—	Binary Systems of Alumina with Silica, Lime and Magnesia	Shepherd, Rankin and Wright	American Journal of Science	United States	Pamphlet
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1909	—	Conductivity, Porosity and Gas Permeability of Refractory Materials	Wologdine and Que- neau	Electrochem & Metallurg. Industry	United States	Cutting
1910	—	Investigations concerning Quartzite ...	Wernicke and Wildschrey	Tonindustrie Zeitung	Germany	Cutting
1910	—	Quartzite and Its Application in the Refractories Industry	Wernicke and Wildschrey	Tonindustrie Zeitung	Germany	Cutting
1910	—	Die Verschiedene Arten den Verwitterung	van Bemmelen, J. M.	Zeits. Angewandte Chemie LXVI	Germany	Cutting
1911	—	The Chemical Constitution of the Kaolinite Molecule	—	Trans. Engl. Ceramic Soc.	Great Britain	Pamphlet
1912	—	An Apparatus for the Determination of the Expansion Coefficient of Solid Bodies	Bock, P. A.	Transactions American Ceramic Society	United States	Pamphlet
1912	—	Notes on Load Tests made on Magnesite, Chrome and Silica Brick	Brown, G. H.	Trans. Amer. Ceramic Society	United States	Pamphlet

TABLE II (continued).

Date.	Title.	Author.	Publication.	Country.	Description.
I. Miscellaneous (continued).					
—	1913 Volume Change of Some Ceramic Raw Materials on Burning	—	Silikat Zeitschrift	Germany	Cutting
—	December 1913 Refractories in the Iron and Steel Industry	Croft, H. W.	Iron Trade Review	United States	Cutting
—	1914 Binary System MgO-SiO ₂ ...	Bowen and Anderson	Amer. Journal of Science	United States	Pamphlet
—	1914 Determination of Mineral and Rock Densities at High Temperatures	Day, Sosman and Hostetter	Amer. Journal of Science	United States	Pamphlet
—	1914 The Ternary System Diopside-Forsterite-Silica	Bowen, N. L.	Amer. Journal of Science	United States	Pamphlet
—	1914 Thermal Conductivity of Refractory Materials	Goerens and Gilles	Ferrum	Germany	Cutting
—	1914 Specific Heats of Refractory Products	Steger	Silikat Zeitschrift	Germany	Cutting
—	1914 Thermal Conductivity of Refractory Building Materials	Heyn, E.	Stahl und Eisen	Germany	Cutting
—	1914 Relative Thermal Conductivities of Silica and Clay Refractories...	Brown, G. H.	Trans. Amer. Ceramic Society	United States	Pamphlet
—	1914 Relative Thermal Conductivity of Silica and Clay Brick	Marshall, S. M.	Metallurgical & Chemical Engineering	United States	Cutting
24 April	1915 Fibrox ...	Weintraub, E	American Electrochem. Society	United States	Pamphlet
—	1915 The Ternary System CaO-Al ₂ O ₃ -SiO ₂	Rankin and Wright	Amer. Journal of Science	United States	Pamphlet
—	1915 Thermal Conductivity of Refractory Materials	Dougill, Hodsman and Cobb	Journal Society of Chemical Industry	Great Britain	Pamphlet
—	1915 Thermal Conductivity of Refractories	Dudley, Jr., Boyd	Transactions American Electrochem. Society	United States	Pamphlet
4 April	1916 The Common Refractory Oxides ...	Sosman, Robert B.	Amer. Chemical Society and American Electrochem. Society	United States	Pamphlet

Material.	Source.
Silver Sand	Holland
English Silica Sand ..	Leighton Buzzard ..
Scotch Silver Sand ..	Glenboig
French Sand	France
Red Sand	Workshop
Yellow Sand	Workshop
Silica Rock	Holyhead
Raw Ganister	Sheffield
Calcined Ganister ..	Sheffield
Scotch Fireclay	Glenboig
Fireclay	Sheffield
Silica	Dinas
Magnesite	—
Chromite	—
Dolomite	—
Carbofrax	Niagara Falls
Refrax	Niagara Falls
Bauxite Brick	—
Silica Brick	—
Specimens of Materials used in Manufactur- ing Sheffield Clay Crucibles, including :—	
(a) China Clay
(b) Derby Clay
(c) Ordinary Clay
(d) Coke Dust
Sheffield Clay Crucible, with lid (new and befo	(after use).
Graphite Crucible, with lid (new and before us	(after use).
Plumbago Stopper and Nozzle showing the cor	
Fireclay
Magnesite

TABLE III.

Specimens of Refractories Exhibited at the Meeting of the Faraday Society on the 8th November, 1916.

Material.	Source.	Analysis.						Loss on Ignition and H ₂ O %	Used for	Remarks.
		SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	MnO %			
A. Sands.										
Silver Sand	Holland	98.30	.70	.40	.80	.20	—	—	Open-hearth furnace.	This material is now replacing the Belgian and Dutch Sands. Photomicros of all these sands are shown in Figs. 5, 6, 7, 8, 11, 12 and 13.
English Silica Sand ..	Leighton Buzzard ..	98.90	.80	—	—	—	—	—	" " " Foundry work. "	
Scotch Silver Sand ..	Glenboig	99.40	.60	—	—	—	—	—		
French Sand	France	82.90	7.00	4.70	1.10	.76	—	—	" "	
Red Sand	Worksop	87.50	5.65	2.57	.82	1.22	.18	1.95	" "	
Yellow Sand	Worksop	92.90	3.90	1.10	.20	.36	—	1.07	" "	
B. Silica and Ganister.										
Silica Rock	Holyhead	95.10	1.30	1.15	.76	.50	Tr.	—	Foundry work	Open-hearth, Converter, and other steel-making furnaces.
Raw Ganister	Sheffield	91.80	3.00	.72	1.43	.75	—	2.80		
Calcined Ganister ..	Sheffield	—	—	—	—	—	—	—		
C. Fireclay.										
Scotch Fireclay	Glenboig	62.00	28.00	2.50	.50	.50	Alkalies .50	6.50	—	Photomicro shown in Fig. 10.
D. Bricks.										
Fireclay	Sheffield	62.90	32.70	3.50	.90	.40	—	—		*This exhibit is a specimen of an insufficiently burnt Silica Brick.
Silica	Dinas	95.80	1.30	1.90	—	—	—	—		
Magnesite	—	2.00	1.30	7.70	8.00	80.00	—	—		
Chromite	—	5.20	13.90	16.20	.78	9.22	Cr ₂ O ₃ 53.66	—		
Dolomite	—	3.30	—	—	53.50 SiC.	36.00	—	—		
Carbofrax	Niagara Falls ..	18.60	4.83	—	77.00	—	—	—	—*	
Refrax	Niagara Falls ..	6.85	3.60	—	89.50	—	—	—		
Bauxite Brick	—	—	—	—	—	—	—	—		
Silica Brick	—	—	—	—	—	—	—	—		
E. Crucibles.										
Specimens of Materials used in Manufacturing Sheffield Clay Crucibles, including:—										
(a) China Clay		46.92	38.56	1.48	.25	.33	—	11.92		
(b) Derby Clay		48.10	34.85	2.75	.20	.75	—	11.99		
(c) Ordinary Clay		44.70	37.50	1.50	1.10	—	—	14.20		
(d) Coke Dust		Fixed C.	87.0	Hydro. C.	2.0	Ash	8.0	H ₂ O	3.0	S. in ash 1.0.
Sheffield Clay Crucible, with lid (new and before use).										
" " " (after use).										
Graphite Crucible, with lid (new and before use).										
" " " (after use).										
F. Stoppers and Nozzles for Ladles.										
Plumbago Stopper and Nozzle showing the condition after casting 15 tons of steel (40 separate taps).										
Fireclay	"	"	28	"	"	(77	"	"	")
Magnesite	"	"	28	"	"	(77	"	"	")

TABLE IV.
English Refractories.

Name of Refractory.	Source.	Analysis.							Analysis made by	
		SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Alkalies.	Loss on Ignition and H ₂ O.		TiO ₂ .
Midlands.										
Silver Sand	—	98.2	0.85	0.55	0.57	0.37	—	0.15	—	Hadfield
Ganister ...	Sheffield ...	91.8	3.00	0.72	1.53	0.75	—	2.80	—	Hadfield
Moulding Sand	Workshop ...	86.7	7.13	1.67	0.54	1.00	—	2.30	—	Hadfield
Fire-clay ...	Stourbridge	65.0	22.0	2.0	0.50	—	0.50	10.0	—	Searle
Fire-clay ...	Shropshire	59.0	27.0	1.0	0.50	—	0.50	12.0	—	Searle
Firebrick ...	Stourbridge	69.0	27.30	1.86	0.27	0.32	—	—	—	Harbord
Firebrick ...	Leeds ...	78.35	13.46	4.40	2.32	1.80	—	—	—	Hadfield
Firebrick ...	Leeds ...	31.01	60.36	4.03	0.72	0.41	—	1.08	2.87	Hadfield
Firebrick ...	Stannington	62.00	32.70	3.50	0.90	0.40	—	—	—	Hadfield
Calcined Magnesite	Liverpool	0.80	—	1.85	2.50	94.40	—	—	—	Hadfield
Raw Magnesite	Liverpool	0.46	0.52	0.52	1.60	46.88	—	—	—	Hadfield
Dolomite Brick ...	Workshop ...	3.30	—	—	53.50	36.00	—	—	CO ₂ 49.5	Hadfield
Magnesite Nozzle	Farnley ...	4.54	1.45	1.36	4.56	87.69	—	0.40	—	—
Wales.										
Dinas Sand	Dinas ...	98.00	1.00	1.00	—	—	—	—	—	Searle
Kidwelly Sand ...	Kidwelly ...	97.2	0.60	1.00	0.28	0.32	—	—	—	Hadfield
Ganister ...	Kidwelly ...	95.5	2.00	0.46	0.66	0.54	—	0.70	—	Hadfield
Fire-clay ...	Holyhead	48.06	44.04	1.26	—	—	—	0.14	4.60	Hadfield
Firebrick, Dinas ...	Dinas ...	95.81	1.34	1.86	—	—	—	—	—	Hadfield

TABLE V.
Foreign Refractories.

Name of Refractory.	Source.	Analysis.						Analysis made by.	
		O ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Alkalies.		Loss on Ignition and H ₂ O.
<i>Germany.</i>									
Herzogenrath Sand	—	98.30	1.50	0.70	Trace	0.32	—	—	—
Raw Ganister ...	Westphalia	95.60	1.76	2.14	0.32	0.20	—	—	—
Fire-clay ...	Coblenz ...	48.10	33.22	2.68	0.86	0.32	—	16.00	—
Fire-clay ...	Grusonwerk	43.80	34.54	0.76	1.03	0.70	—	19.50	—
Fire-clay ...	Krupp	68.0	24.55	2.50	0.85	—	1.30	0.10	2.00
Magnesite Brick ...	Schweidnitz	1.20	1.30	7.50	4.50	85.20	—	—	—
Calcined Magnesite	Coblenz	4.30	0.40	11.00	4.10	80.30	—	—	—
Magnesite Brick ...	Coblenz	2.23	1.29	7.91	11.07	73.48	—	—	0.23
<i>France and Belgium.</i>									
Glass Sand	Belgium ...	98.3	0.70	0.40	0.80	0.20	—	—	—
Moulding Sand	France ...	85.8	6.80	2.40	0.82	0.50	—	3.50	—
Moulding Sand	France ...	82.9	7.00	4.70	1.10	0.76	—	—	—
Calcined Magnesite	France ...	—	—	—	—	83.50	—	—	—
<i>American.</i>									
Silica Sand	Cheshire, Mass., U.S.A.	97.80	1.06	0.30	0.45	0.32	—	—	—
Silica Sand	High Bridge, N.J.	96.75	1.45	1.05	0.57	0.25	—	0.50	—
Ganister ...	High Bridge, N.J.	93.25	3.89	0.86	0.42	—	—	1.16	—
Moulding Sand	Newport, U.S.A.	81.60	6.10	4.85	1.11	1.15	—	3.30	—
Moulding Sand	New York, U.S.A.	80.60	10.40	4.36	1.20	1.00	—	2.30	—
Moulding Sand	High Bridge, U.S.A.	82.40	6.08	2.12	0.82	1.50	—	7.10	—
Fire-clay ...	Mineral Point, O., U.S.A.	52.52	31.84	0.67	0.50	0.19	0.59	11.68	1.68
Fire-clay ...	Woodbridge, N.J.	51.56	33.13	0.78	Trace	Trace	Trace	12.50	1.91
Fire-clay ...	New Brighton, Pa.	62.89	21.49	1.81	0.38	0.56	2.52	8.74	1.82
Succa Sunna Sand	High Bridge	96.75	1.45	1.05	0.57	0.25	—	0.50	—

TABLE VI.
Chrome Iron Ore.

Nature of Material.	Analysis.						Remarks.
	SiO ₂ .	Al ₂ O ₃ .	Iron Oxides.	CaO.	MgO.	Cr ₂ O ₃ .	H ₂ O.
Chrome iron ore ...	2.25	3.01	35.82	4.20	2.60	51.54	—
	2.00	19.25	14.70	3.75	17.66	41.67	0.97
						Harbord	Typical analysis
						Macfarlane	Typical analysis

Chrome Bricks, Bauxite Bricks.

Nature of Material.	Analysis.								Remarks.	
	Analysis Made by.									
	SiO ₂ .	Al ₂ O ₃ .	Iron Oxides.	CaO.	MgO.	Cr ₂ O ₃ .	H ₂ O.	TiO ₂ .		
Chrome brick ...	5.20	13.90	16.20	0.78	9.22	53.66	—	—	Macfarlane	Typical analysis Sample from Schweidnitz
	13.60	14.88	15.72	—	—	27.65	—	—		
Bauxite brick ...	3.50	51.40	38.37	2.46	0.79	—	—	3.08	Macfarlane Macfarlane	Typical analysis Typical analysis
	35.80	55.80	3.40	0.90	—	—	—	—		

TABLE VII.

Titanium Ores.

(From Rare Earth Industry, Johnstone.)

	PICOILMENITE.		ILMENITE.		SPHENE.	STRUIVERITE.
	Ceylon.		Caroline.	Ilmen Mountains.		
	Per cent.		Per cent.		Per cent.	Per cent.
TiO ₂	64.72	...	52.75	45.93	40.82	45.74
FeO	16.59	...	33.08	36.52	—	8.27
Fe ₂ O ₃	2.66	...	8.08	14.30	—	—
CaO	—	...	—	—	28.08	—
MgO	15.76	...	5.33	0.59	0.40	—
SiO ₂	0.70	...	—	—	30.10	0.20
MnO	0.42	...	—	2.72	—	Trace
Nb ₂ O ₅	—	...	—	—	—	35.96
Ta ₂ O ₅	—	...	—	—	—	2.67
SnO ₂	—	...	—	—	—	0.50
Water	—	...	—	—	0.54	—

Zirconium Ores.

(From Rare Earth Industry, Johnstone.)

	ZIRCON.		BADDELEYITE.			
	Ceylon.	Norway.	Brazil : Glassy Variety.	Brazil : Stony Variety.	Brazil : Pebbles.	Brazil : Com- mercial Variety.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
ZrO ₂	66.35	64.05	94.12	88.40	74.48	68.93
Fe ₂ O ₃	0.83	2.85	3.22	4.07	10.26	3.59
TiO ₂	—	—	0.98	3.12	1.35	0.60
CaO	—	—	—	—	—	—
SiO ₂	32.35	32.53	2.41	5.89	14.08	26.30
H ₂ O	0.23	—	—	—	—	0.80
						Ceylon.
						Per cent.
						98.90
						0.82
						—
						0.06
						0.19
						0.28

TABLE VIII.

Carborundum, Graphite.—Carborundum Bricks.

	SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	SiC.	Analysis Made by
"Carbofrax" Brick...	18.60	4.83	77.0	Hadfield
"Refrax" Brick ...	6.85	3.60	89.50	Hadfield

Analysis of Used Graphite Crucible.

						Per cent.
Free carbon	38.92
Silicon carbide	20.14
Iron oxide (FeO)	4.37
Alumina	15.11
Free silica	20.47
Lime	0.98

(From Johnson, *Analysis of Special Steels, Steel Making Alloys, and Graphites.*

TABLE IX.

Photo- micro Fig. No.	Description.	Source.	Remarks on Photomicrograph.
5	Yellow Sand ...	Worksop	(Not treated with HCl) The effect of the colouring matter on the grains is very clearly shown on comparing them with the photographs of the silver sands. The grains are generally very rounded and of about the same size as the Scotch silver sand.
6	Yellow Sand ...	Worksop	(After treatment with HCl) Medium and small-sized grain of well rounded form.
7	Silver Sand ...	Holland	The grains are shown to be very regular in size and smaller than either Scotch or Worksop sand.
8	Scotch Silver Sand	Glenboig	White, almost transparent grains of irregular size. The grains are distinctly coarser than those of the Dutch silver sand, and generally more angular in form.
9	Back Facing Sand	—	The sand as seen by the naked eye has a dark grey-brown colour. The microscope shows this sand to consist of many-sized grains of various colours, from transparent ones to those quite black and opaque.
10	Scotch Fire-clay...	—	Light grey amorphous material. This, it must be remembered, has been ground.
11	Red Sand ...	Worksop	A fine grain mixed with a medium-sized one—two distinct sizes clearly marked.
12	Sand ...	Leighton Buzzard	Well rounded grains of large and uniform size.
13	Red Sand ...	France	Very small grains—very uniform; many are transparent and of angular character.

REFRACTORY MATERIAL.

By FREDERICK J. BYWATER.

(*Reprinted by kind permission from the TRANSACTIONS OF THE INSTITUTION OF GAS ENGINEERS, 1908, as a Contribution to the present GENERAL DISCUSSION.**)

The absence from the "Transactions" of the Institution of any paper dealing with the subject of refractory material, and the general scarcity of technical literature on the question, would provide ample apology, were one needed, for bringing it forward for consideration.

The suitability of materials offered by manufacturers for use in the construction of retort-settings is one which comes up for decision annually, and its importance, which has never been underestimated by gas engineers, is one which is increasing year by year. The causes of this are several. The introduction and improvement in the efficiency of gaseous firing have made higher temperatures of carbonization possible. These possibilities, coupled with the almost general reduction in illuminating power, have been taken advantage of by most engineers; and the average temperature of carbonization may now safely be stated to be at least 200° Fahr. higher than it was twenty years ago. This fact, together with the development of new carbonizing systems, particularly by that of inclined retorts, has caused more attention to be given to these matters, by reason of the greater demands made upon the materials of construction in retort-settings.

Whether these demands have been adequately met by improvement in the quality of material, is a question of local rather than of general application, according to the source from which the refractory material is obtained. Yet, despite the fact that knowledge of the raw materials is, or should be, greater than it was twenty years ago, and that new and extensive sources of highly refractory material have been opened up during this period, it is a matter for very grave doubt whether, on the whole, the quality of firebrick and retort material has generally improved.

Absolutely refractory material, in the true sense of the word, does not exist; the term refractory being merely a relative one, depending upon the process in which the material is to be employed. The subject is therefore one of exceedingly wide application, involving as it does material used in most metallurgical and chemical processes, each of which requires to be studied separately before a suitable material can be chosen.

To treat this question thoroughly, and in all its many and interesting phases, would be quite impossible and out of place here. The author therefore proposes to deal with it as it affects gas engineers only. It is not intended either to treat in detail the question of manufacture (which can be much better studied if required by a visit to an up-to-date works) or the very intricate chemical problems which present themselves for solution in studying the subject, and which probably belong to other circles; but rather to set

* *Being on active service, the author has been unable to revise this Paper for the purpose of this reprint.*

forth the general principles underlying the composition and utility of the principal refractory agents employed in retort-settings, and indicate the lines on which it would appear that present-day requirements are likely to be most successfully met.

The chief sources of refractory material at present employed in the construction of retort-settings are : (1) fire-clays ; (2) silicious quartz.

ORIGIN OF FIRE-CLAYS.

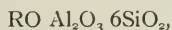
The origin of fire-clays is a question around which much wordy warfare has been waged ; but from the investigations of Bischof, Forchhammer, and others, the origin of kaolin, or china clay, of which fire-clays are really an impure form, may be ascribed to the decomposition by weathering of feldspar or minerals related to it.

By weathering is understood the process of destruction of a rock, in which, through external chemical and physical influences, a part of the substance is removed, and thereby a lessening of the cohesion is brought about ; so that it is possible for mechanical forces to carry away the more or less changed residue and deposit it elsewhere to form new strata. This process of destruction of the rocks forming the earth's crust, by the influence of water in union with oxygen, carbonic acid, and change of temperature, is constantly going on, and causing at the same time new formations to appear. Owing, however, to the diversity of the chemical and physical properties of the masses subjected to change, and also to the fact that the destruction is so frequently modified by local conditions, a vast number of new forms arise, and offer such infinite difficulties to their consideration from common points of view, that science has not yet completely succeeded in bringing into this chaos that clearness which would enable industries to use readily, and with entire confidence, all the materials at disposal.

Only a few of the crystalline rocks can, from their chemical composition, produce clay on weathering ; and rarely do the clay-forming rocks undergo the process of weathering to the last stage—the formation of true clay substance or kaolin—but remain more or less in the intermediate stage. Besides clay, therefore, there arise detritus, gravel, sand, loam, etc., or, if the process of weathering and destruction be interrupted, the original rocks may be re-formed as sandstones, shales, etc., and perhaps crystalline rocks.

Feldspars have been investigated very thoroughly with regard to the process of weathering, and although, by reason of the great resistance of crystalline rocks to the weak action of the forces at work, the weathering process occupies a very long time, and thereby makes difficult the study of the phases through which it runs, it is now possible to make a fairly accurate general statement as to what has taken place.

Feldspar is not a single chemical compound, but a term used to denote a group of mineral silicates, with many varieties of similar composition. Probably the best known is orthoclase or potassium feldspar, which would contain, when pure, 64·7 per cent. of silica, 18·3 per cent. of alumina, and 17 per cent. of potash. The potassium may, however, be partially or entirely replaced by any one of several other metals, such as sodium, calcium, and lime ; and in each case the new mineral retains the family name of feldspar. They may all be represented by the general formula—



where RO represents 1 molecule of oxide, similar to potash, soda, or lime, Al_2O_3 1 molecule of alumina, and 6SiO_2 represents 6 molecules of silica.

The decomposition of the feldspathic constituent of crystalline rocks begins, as a rule, superficially, and shows itself in a dimming of the crystal surface. Under the microscope such a crystal in the first stage of weathering is seen to be traversed by numerous very fine cracks, more or less deep. When subjected to washing by rain water—i.e. water with carbonic acid dissolved in it—the alkalis, lime, and silicic acid are carried away, and the mineral would suffer a loss of about 50 per cent. by weight and 33 per cent. by volume on being transformed into clay. This, on a small scale, is an example of what has taken place in the formation of fire-clays; the surfaces of huge masses of feldspathic rocks, subjected for centuries to the influence of weather—frost, snow, rain, and alternations of temperature—have been first of all broken up, and either converted into clay substance *in situ*, or more usually washed away and deposited elsewhere. After the completion of the weathering and washing process, which the original rocks from which clay has been derived undergo, the chemical effect of the water and atmospheric agencies does not cease. Further weathering or lixiviation takes place; the formation of the clay substance being considerably assisted by the continual rubbing and breaking-up of the felspar granules against other and harder minerals in the presence of water—some of the substances being dissolved. And just as in the case of weathering we can follow the breaking-down of the crystalline rocks, so also, by an inverse metamorphosis and infiltration, we can pass from the detritus of the weathering process back again to the solid rocks, sandstones, etc., and also fire-clay seams.

Where the products of the weathering action are not washed away, but still remain on the same site, the original rocks, split up first of all into thin laminæ, becoming thinner and thinner, again take, on re-formation, the structure of the rock from which they come, even though considerably distorted by loss of substance and volume. If, however, in addition to the weathering, a washing has taken place, the structural relations of the clay become much different.

These sedimentary clay beds most frequently assume a horizontal parallel structure, caused by the presence of layers which are chemically and physically different to others near by; so that at different heights of the deposit or seam, sand, felspar, or clay predominates, which themselves are different with reference to grain and plasticity on the one hand, and, on the other, show difference in the mineral detritus—the crystalline residue appearing in extremely thin laminæ, in which the weathering process has not progressed to the complete extraction of the alkalis, and the loss of crystalline texture always associated with it.

This is readily seen on reference to the large detailed cross section of the so-called Old Mine Seam of Stourbridge clay, which is fairly typical of such action. Here the "mild" clay, rich in alumina, predominates at the top of the seam, gradually changing to the "strong" or silicious clay at the bottom, with the "medium" clay in between. This "medium" strata usually contains the well-known Stourbridge "Pot" clay.

To what cause this stratification is due cannot be definitely stated, owing to lack of positive and comparative observations; but it may be said that the silicious crystalline strata are undoubtedly formed in agreement with the general law of crystal formation, and the action of water has been a very potent factor throughout.

When examined under the microscope, the strong clay is seen to consist of well-defined crystalline forms; the medium clay has some such crystals in a mass of fragmentary shapes; and the mild clay seems to be wholly made up of irregular forms of very fine particles of matter. It would appear that

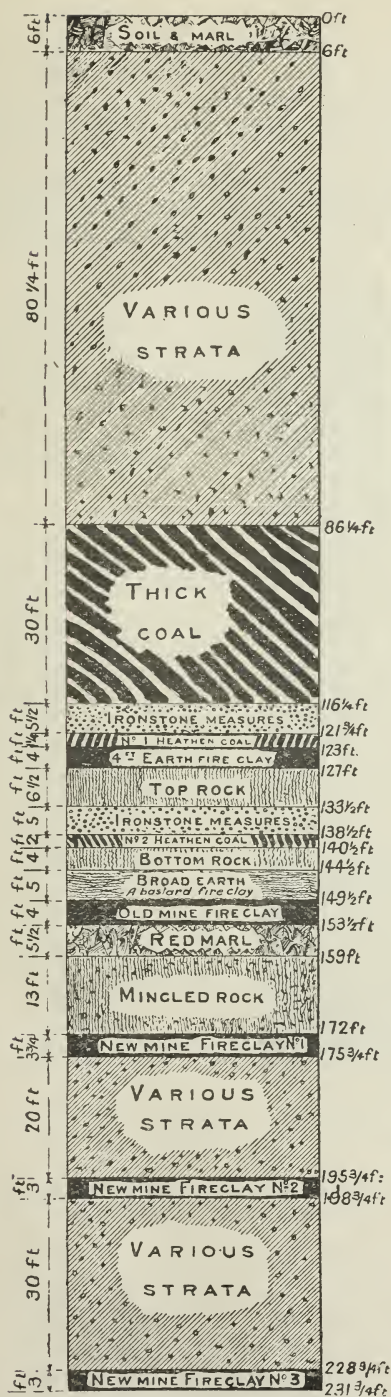


FIG. 1.—Typical Chart of Stourbridge Seams.

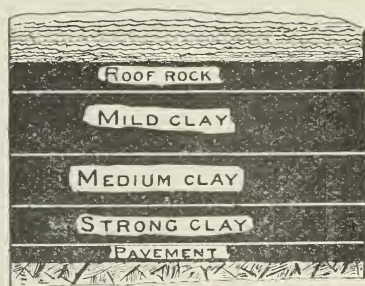


FIG. 2.—Enlarged Section of Stour-
bridge Clay Seam.

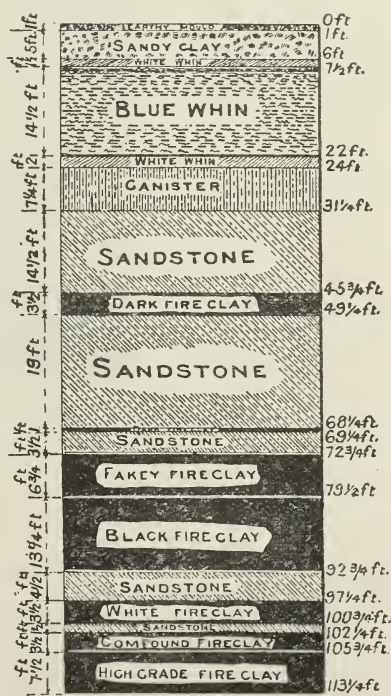


FIG. 3.—Chart of Fire-clay Seams at Glenboig.

these latter have had their crystalline forms broken up by the washing and weathering, and the strong clays have not suffered in this way. The mild clays are more plastic, and make stronger and tougher bricks than the latter. In this there seems to be a close correspondence between fire-clays and many metals, notably iron, in which the tensile strength decreases as the crystallization increases.

With regard to the fire-clays of the coal measures, of which type there are many existing in this country, it would appear, from the stigmata existing in some of them, that they were the original soils on which grew the vegetation

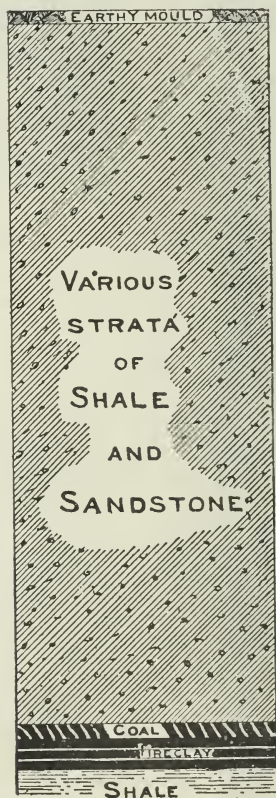
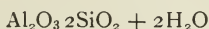


FIG. 4.—Chart of South Yorkshire Fire-clay Seams.

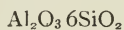
that formed the coal; but they are not always associated together now. In some instances they occur in the coal itself, and in some apart, in which case the coal may have been eroded away, or may never have been formed. The growth of vegetation, and the leaching action of water generally associated with it, would undoubtedly remove some of the alkalis from the clay; and the carbonic acid resulting from its ultimate decay would materially assist in the removal of impurities. The dark grey colour of the coal measure clays is due to minute particles of organic matter disseminated throughout the clay by the action of water; and the other colorations—blue, black, red, etc.—that occur are due to mineral impurities.

COMPOSITION OF FIRE-CLAYS.

Having now traced their origin, it is possible to proceed to discuss the chemical and physical composition of fire-clays. It will be understood that in the washing and weathering which gives them origin, the clay products must lose a considerable amount of the alkali molecule originally present ; and where the weathering of the original feldspathic rock has been complete, kaolins are formed, and fire-clays result where the weathering has been incomplete or interrupted. Kaolin may be represented by the formula :



corresponding to 46 per cent. of silica, 40 per cent. of alumina, and 13 per cent. of water. This may be regarded as the true clay substance, and is the most refractory combination of silica and alumina that exists. Such a complete result is rarely attained, however ; and the intermediate fire-clay is more often the product as at present known. Fire-clays may be represented by the general formula :



corresponding to 60 per cent. of silica and 20 per cent. of alumina, together with a varying amount of water, and small, but important, remnants of their original mother rocks or extraneous deposits in the shape of lime, potash, soda, and iron, all of which are impurities, and exercise a most deleterious effect on the refractoriness of the clay if present in excess. The cause of this is that the silicates of these bases are far more fusible than that of alumina ; and often their presence results in the formation of multiple silicates, which are still more fusible when subjected to even moderately high temperatures. But the whole question of the relation which the refractoriness of clays bears to the chemical constituents is a most intricate one ; and it cannot be said that any very determined efforts have been made in this country towards their solution.

The general practice has been to consider the refractoriness to be in direct ratio to the percentage of silica present, as found by ultimate analyses, and the absence of impurities, iron, lime, alkalis, potash, soda, etc., which are usually limited in the aggregate to about 3 or 4 per cent. Such an assumption is, however, an accurate one only within certain limits.

So far as the author is aware, the German chemists Richter and Bischof were the first to attempt to establish a relation between the composition of fire-clays and their refractoriness ; and in the latter's treatise on the subject, he enunciates a law for expressing the refractory character of clays by a numerical coefficient based on the relation of the silica and alumina to each other, and to the other fluxing bases, as found by analysis. This law, however, proved quite unsatisfactory when applied to other clays than those tested by Bischof ; and after much investigation, Seger substituted a modified formulâ, to read :

$$\text{Refractory quotient} = (A + B) \frac{A}{B},$$

where A represents the ratio of alumina and B that of silica to the fluxes taken as unity. But the author has found this formula of little use in arriving at definite conclusions as to the refractoriness of any clay, as compared with another from a different mine ; and Seger himself eventually restricted its use to relative comparisons and for determining the refractoriness of various silicates of alumina.

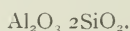
All the evidence collected tends to show that great difficulties are encountered in attempting to establish a relation between the composition and fusibility of clays from investigations based on the ultimate analysis. It is possible, however, to arrive at more definite conclusions. But in order to do this, some other methods of examination must be pursued than those usually employed which proceed to investigate fire-clays by complete analyses. As an instance of the futility of the latter method, the following is an example of an analysis of a Stourbridge clay of medium quality :

Silica	64.62 per cent.
Alumina	21.65 "
Ferric oxide	1.48 "
Lime	1.88 "
Magnesia	0.62 "
Moisture	9.62 "

This clay does not make satisfactory firebricks, but why this is so is not revealed by the analysis. The latter gives no information as to the condition in which the silica is present in the clay. It may exist as quartz, or in combination with alumina ; and these different states have a great effect on the refractoriness. A complete analysis, of course, shows the amounts of iron, alkalis, lime, etc., and so to some extent indicates its properties ; but these depend also very considerably on the combination of the elements, and on the physical form of the mineralogical constituents. Such an analysis assumes clay to be a homogeneous chemical compound, which it most certainly is not ; and from what has been said of their formation, it will be understood, without further pursuing the matter, that they are, instead, mechanical mixtures of the various processes of weathering.

Fire-clays really consist of mixtures of

- (1) True clay substance (the result of complete weathering) approximating to the formula



- (2) Quartz (as sand of various sized grain), SiO_2 .
- (3) Felspathic remnants of the original rocks. $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$.

It does seem striking, on reflection, to throw all these very dissimilar substances into the same pot after dissolving them up, and to proceed to an investigation which takes no regard whatever of their differences. By separating the clay into its mineralogical constituents, on the above-mentioned lines, a far more accurate estimate can be made as to its value. A better knowledge will be obtained of the inner constitution of the clays, and of the distribution of its constituents—which of them do not weather at all, such as quartz, which belong to constituents capable of weathering, as the mineral felspar fragments, and which to the real clay substance in the widest sense. Such a separation can be effected by the decomposition and solution of the clay substance (kaolin) by hot sulphuric acid and sodium hydrate. Alumina is determined in the remainder so as to estimate felspar ; while the quartz is determined by difference.

The subjoined analyses (p. 39) of three clays show that they may be similar in composition when analysed by the one method, but entirely different by the other, or both may give similar results.

					A.	B.	C.
					Per cent.	Per cent.	Per cent.
SiO ₂	60.49	62.52	56.14
Al ₂ O ₃	26.10	25.57	30.99
FeO	2.11	0.92	0.80
CaO	trace	0.65	nil
MgO	0.56	0.10	0.27
Alkalis	1.08	1.04	0.78
Loss on ignition	9.80	9.27	11.27
Clay substance	71.54	72.05	79.47
Quartz	25.97	27.78	18.92
Felspar	2.49	0.10	1.61

The clay substance is highly refractory, and its presence usually indicates a refractory clay. The effect of quartz is variable; but in the absence of felspar, and when the grains are not very small, it tends to increase refractoriness. If much felspar is present, the fusion-point is lowered, as will be understood from its alkali constituents.

To complete the investigation of the clay on these "rational" lines, a mechanical analysis is also most helpful. This can be effected by a special washing apparatus, such as that devised by Shoene. After boiling, a given weight of clay is placed in this apparatus, and a stream of water of definite speed is allowed to pass through and wash out the finer particles. By working at various speeds, particles of various sizes and characteristics are obtained separate from each other. In this manner the clay may be divided up into clay substance, silt, dust sand, fine sand, and loam sand; and if, then, different portions are analysed, further clues are obtained as to the best methods of handling the clay before use. Thus it has been found by experiment that quartz sand acts as a flux when it is in an exceedingly fine state—so fine, in fact, that it cannot be separated from the clay substance by washing. Coarser particles increase the refractoriness. Other facts of the utmost importance, if a true estimation of the value of a fire-clay is to be arrived at, are revealed by such an investigation, for, having divided up the substance in this manner, investigation by ultimate analysis is now permissible.

Of the relative merits, as refractory agents, of the clay substance (or kaolin) and quartz, separated as above, it has been found as the result of extensive experiments by Bischof, Seger, and others, that alumina is slightly more refractory than silica, and that, mixing silica and alumina in various proportions, the composition $\text{Al}_2\text{O}_3 : 2\text{SiO}_2$ —i.e. kaolin or true clay substance—is the most infusible. The addition of silica increases the fusibility until the composition $1\text{Al}_2\text{O}_3 : 17\text{SiO}_2$ in chemical equivalents is reached; and with further increase of silica the refractoriness rises. This is represented graphically in the subjoined diagram (Fig. 5).

The curve illustrates the effect of the addition of silica on fusibility, and also that when there is no alumina present the refractoriness rises to $3,326^\circ$ Fahr.—the melting-point of pure silica. It should be noticed that the melting-point of pure silica is slightly less than that of the pure clay substance. The position of a clay in the refractory scale depends, however, not merely on the ratio of alumina to silica, but mainly on the amount of accompanying fluxes, iron oxides, lime, magnesia, potash, and soda. Extensive experiments carried out by Bischof and Richters seem to show that the

substances act as fluxes in the ratio of their equivalent combining weights—i.e. 20 parts of magnesia will have the same effect as 28 parts of lime, 36 parts of ferrous oxide, etc.—and that they exert a greater fluxing action on the clay when it is high in silica than when it is high in alumina.

Reverting again to the more rational methods of investigating fire-clays, it is a matter for regret that firebrick manufacturers do not avail themselves more of the great value of such analyses. The author has visited many works in this country, but has never yet found anywhere such investigations being carried out; the methods employed in many cases being very primitive.

If, from time to time, new clays are met with, pieces are taken from the top, middle, and bottom of the seam, and burnt on the curtain wall of a kiln. If this reveals certain satisfactory evidences, other pieces may be placed in a cutting heat on the bridge of a reverberatory furnace; and if this test still proves satisfactory, the clay may be subjected to weathering, and eventually made up into bricks, and very often the buyer unwittingly completes the manufacturer's knowledge of the new material by his complaints or satisfaction as the case may be!

In some cases clay samples and bricks are submitted to analytical chemists from time to time; but the number of works possessing a scientific

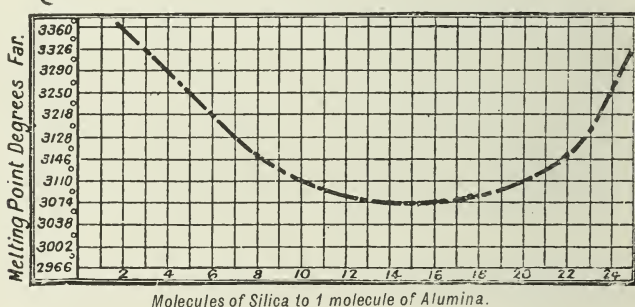


FIG. 5.

staff is exceedingly few. This is very surprising, considering the intricacies of the raw material and the vast interests concerned.

To sum up, then, it may safely be stated that the ultimate analyses of a clay, as usually employed, are of very little use in arriving at a proper estimate of refractoriness, and that far better knowledge is that based on mechanical and rational methods for subdividing it into its various mineralogical constituents, when ultimate analyses may be employed. Having arrived at a true knowledge of the constituents of the clay on these lines, samples and mixtures may be tested with success in a practical way in a small furnace such as those to be described later.

COMPOSITION OF FIREBRICKS.

Having dealt with the question of the constitution of fire-clays, and the effect this has on their fusibility, the finished product may now be discussed. As a general statement, it is, of course, true that, unless the clays are good, the resulting brick material cannot well be expected to be so. But this requires certain qualification. Many clays when mined have a fairly high content of impurities, i.e. alkalis (potash, soda, etc.), lime, and iron—and if bricks be made from the raw clay, the result is disastrous. It is therefore again exposed to the action of the weather, and the process of the complete

reduction of the rock to clay which was interrupted many thousands of years ago is resumed. The chief agents are, again, water and frost. The water sinks into the pores of the clay, reaching the minimum of volume at 4° C., and expands very suddenly on going over to the solid state. The beneficent effect which the freezing process exerts in loosening and disintegrating the clay mass has always been recognized by firebrick manufacturers; and most clays are considerably improved by weathering. If one desires an effective result of the weathering and freezing process, it is very essential to make the layers of clay no deeper than the frost is wont to penetrate into the ground—certainly not more than 2 feet—and to pile it as loosely as possible. If this is done, in addition to improvement in the texture and body of the clays, considerable removal of impurities is effected as seen from the following analyses of samples of the same clay before and after weathering:—

BEFORE WEATHERING.				AFTER WEATHERING.			
Silica	64.62	Silica	64.70
Alumina	21.65	Alumina	22.90
Ferric oxide	1.48	Ferric oxide	1.30
Lime...	1.98	Lime...	1.01
Alkalis	1.62	Alkalis75
Moisture	8.52	Moisture	9.52

The clays which are usually most improved by weathering are the strong clays containing a high percentage of silica and impurities—a class in which, as previously explained, the original weathering process was not carried far enough to break down the crystal form. One notable exception to this general acceptance of improvement by weathering is the well-known Glenboig clay, which appears to be very little improved by weathering. But this is undoubtedly attributable to the high percentage of alumina present, and the small amount of impurities.

After weathering, the clay is taken to the grinding mill, where the requisite mixtures of raw clay are made. Few fire-clays can be used by themselves as mined, even after weathering; the general rule being to make up mixtures of the various clays available—strong, mild, or medium—according to the goods required. A certain percentage of calcined clay, or grog, is also added in varying proportions, for the purpose of reducing shrinkage and opening up the texture of the clay. For retorts and large blocks and tiles, 30 to 40 per cent. is usual, and for 3-in. bricks 15 to 20 per cent.; but these proportions will vary somewhat with the clay used. If too much calcined material be employed, the result will be a brick of loose, coarse, friable nature, lacking strength. The relative sizes of the constituent parts and the mechanical condition of the clay as it leaves the grinding mill have considerable influence on the refractory character of the manufactured brick. The larger the grain the less likely is it to fuse when heated, as the ultimate fusion naturally commences from the outside of the grain of the mineral constituents. Where the grain is small, more intimate and extensive surface-contact is possible, and so complete failure by fusion more often occurs in fine-grained than in coarse-grained material. This is well indicated by the three pieces of retort material shown, all of which are made from the same clay, which is of good quality but of different degrees of fineness—viz.: (1) coarse, (2) moderately coarse, and (3) fine-grained.

The samples have been subjected to a temperature of 2,600° Fahr.; and

whereas the coarse-grained specimen shows very little sign, and the moderately coarse only faint signs of fusion, the fine closely-grained piece shows considerable fusion. Mild dense clays of moderate fusibility sometimes receive, after weathering, an admixture of silica quartz as sand or crushed rock, with the intention of raising their fusing-point; but such an experiment is rarely completely successful.

The finished brick material, after being carefully dried and burnt, should present a cream or buff coloured fracture and external appearance; but the latter is frequently altered by the process known as "flashing," on completion of burning. Bricks burnt in an oxidizing flame are white, and in a reducing flame brown; but the latter coloration may also be due to iron.

The chemical changes consequent on burning are; (1) elimination of all carbonaceous matter; (2) dehydration of the silicates of alumina, destroying their plasticity; and (3) reduction of carbonate or protoxide of iron, converting it into anhydrous sesquioxide, to which the yellow colour of the brick is due. If burning be carried to a high temperature, the yellow colour is replaced by a dull, greyish brown or red, due to the partial reduction of the sesquioxide of iron and its conversion into silicate of the protoxide or minutely disseminated particles of metallic iron. Lightly burnt bricks containing small nodules of iron oxide sometimes reveal the latter by a pink coloration, which gradually darkens to a greenish black as the temperature of burning increases.

Iron is not nearly so dangerous an impurity when the clay is rich in alumina; the highly refractory clay bauxite, which contains 60 per cent. of alumina and 20 per cent. of iron, and only a small percentage of silica, is infusible at very high temperatures. Where intense heat is not to be encountered, and refractoriness with toughness and strength is required, bricks rich in alumina and containing 3 per cent. of iron will give good results. Other fluxes, however, must be absent. Such bricks (i.e. those rich in alumina) exhibit considerable shrinkage when first burnt; but if burnt in the kiln at a high temperature they do not show subsequent shrinkage or variations. Iron oxide should only be allowed in very small quantities in bricks subjected to producer gas and such-like, by which it is reduced. If carbonaceous matter be present to the extent of 1 per cent., the sesquioxide causing the colouring is reduced to the lower oxide, which is preserved as a colourless silicate. If lime and other alkaline earths be present also, the colouring effects of iron are checked by the formation, at only moderately high temperatures, of double silicates of lime and iron. If a fairly large percentage of free silica be present, with 2 per cent. or more alkalis, a dark vitreous combination is formed if burnt at high temperature; but it is possible for alkalis to be present in a firebrick without revealing themselves by colouring effect, and no brick should be accepted for use where high temperatures are to be withstood containing more than a total of 1 per cent. of potash and soda. If temperatures are moderate, 2 per cent. may be allowed, provided other fluxes are low.

From what has been said, it will be understood that it is quite impossible to form a correct judgment of the refractoriness of a firebrick by its colour, though, after considerable experience of the clay goods of any district, it is possible for a practical man to give an approximate opinion of the value of a brick from the appearance of its fracture, providing it is well burnt. This latter should always be insisted on. Hard, clear-ringing, heavy, well-burnt bricks usually prove most refractory and serviceable, other things being equal; and impurities can at all times be more easily detected in a well-burnt brick than in a lightly burnt one. Bricks, during the process of

burning, should always be subjected to as high a temperature as they will be required to withstand in work. Unless this is done, subsequent shrinkage may occur.

HIGHLY SILICIOUS FIRE-CLAYS.

Differing somewhat from the ordinary fire-clays are several highly silicious clays of considerable refractoriness. These usually contain from 85 to 90 per cent. of silica, and a small percentage of alumina and impurities. Such are : (1) the ganister fire-clay of South Yorkshire ; (2) the fire-clay deposits in the limestone hills of Derbyshire and North Staffordshire, etc., and other "deposit clays" in various parts. The first-named has most probably been formed by the disintegration of sandstone ; and the alumina content may have been incorporated from neighbouring clay-forming rocks, or from the same rocks. Such material usually contains—

Silica	88·76 per cent.
Alumina	7·56 "
Oxide of iron	1·55 "
Lime	0·80 "
Magnesia	1·24 "

(Analysis of a piece of ganister calcined clay.)

It is used as mined, without weathering, but with the addition of 25 to 30 per cent. of calcined material. Bricks made of this clay show no sign of

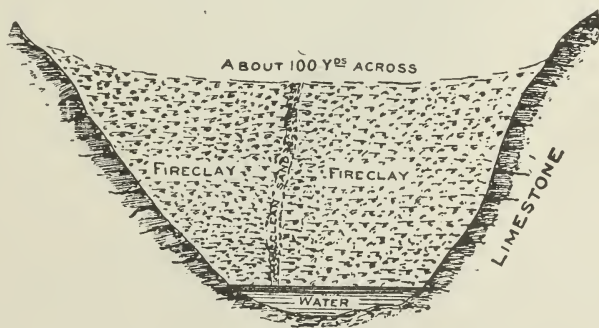


FIG. 6.—Typical Cross Section, showing Fire-clay Deposit in Limestone Hills.

fusing at a temperature of 2,400° Fahr., and are therefore suitable for places in retort-settings where the temperature is not intense. Being of a loose and fine nature, without plasticity, it is unsuitable for making large blocks and tiles ; but ordinary 3-inch bricks are hard and fairly tough.

There are numerous pockets of the second-named clay occurring in irregular hollows in the mountain limestone of Derbyshire and North Staffordshire ; and they are also said to be met with in North Wales and Ireland. The deposit consists of fine white clay and clean sharp sand, sharply separated, together with insoluble remnants from the local dissolution of limestone, intermingled with the *débris* of the overlying millstone grit. Fig. 6 may be taken as a fairly typical cross-section of one of these pockets. Many of them are of considerable width, and of depths running down to the water ; and the supply would appear inexhaustible. An analysis of the raw clay gives :—

Silica	81.21 per cent.
Alumina	11.47 "
Lime	1.27 "
Magnesia	a trace
Iron oxide	1.14 per cent.
Potash and soda	1.58 "
Combined water and organic matter	3.66 "

The clay is "won" by hand, only a sharp pick being required to loosen it. It is used as found in the raw state, after grinding, and without admixture of calcined material. The bricks, which show no signs of fusion at 2,400° Fahr. are of a white, somewhat soft biscuit nature, do not contract or expand on burning, and only very slightly on subsequent heating. The clay is unsuitable for making large blocks and tiles.

Of a somewhat similar class to the above are the deposit clays of Buckinghamshire and Surrey, of which the "Ewell" clay is perhaps the best known, although this latter clay usually contains more silica and iron and less alumina.

SILICA QUARTZ ROCK.

The principal sources of this are in the neighbourhood of the Neath Valley in South Wales, and the "black" or quartz ganister found in the

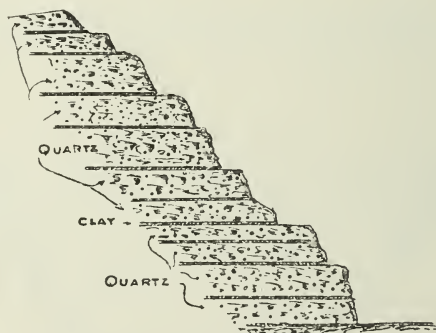


FIG. 7.—Cross Section of a Dinas Quartz Quarry, South Wales.

neighbourhood of Sheffield. The origin of both is traceable to the disintegration of sandstone: and they have very similar composition. Samples of raw material examined have been found to contain:—

DINAS QUARTZ.				BLACK GANISTER.			
97.6	per cent.	of silica		98.5	per cent.	of silica	
0.5	"	"	alumina	0.3	"	"	alumina
1.5	"	"	iron	1.3	"	"	iron
0.2	"	"	lime	0.2	"	"	lime
0.09	"	"	potash	Traces	{		potash
0.03	"	"	soda				soda

The South Wales or Dinas quartz has a pale greyish blue tinge, and is worked in open quarries (see Fig. 7) about 50 to 60 feet high, with thin veins of yellow clay between. The rock is hard, and steam or compressed air drills are used. Very little impurities are found, and the rock is crushed and mixed with 1 to 1½ per cent. of lime and a small percentage of silicious clay

to toughen the brick. The lime causes slight fusion of the granules of quartz, and so binds the whole together. No calcined material is used. The bricks are burnt at about 2,600° Fahr., and expand somewhat on burning and subsequent heating.

“BLACK” GANISTER.

This forms the seatstone beneath certain seams in the lower coal measures near Sheffield (Fig. 8). It is mined by means of rock drills; and the method of manufacture is similar to that of the Dinas quartz brick, except that there are some fairly well-defined impurities found in the raw material, which can be picked out. There is also usually an admixture of 25 per cent. of calcined material or “grog.”

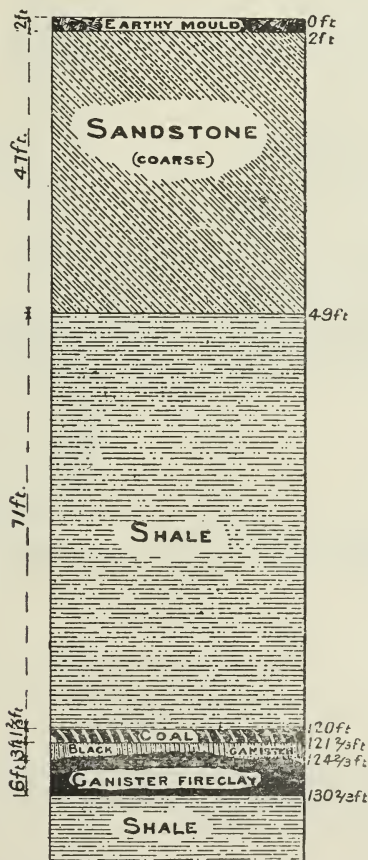


FIG. 8.—Chart of Mine near Sheffield, showing Black Ganister and Ganister.

These highly silicious bricks usually show expansion on heating up, and should not therefore be laid too tightly and with too fine a joint. It is necessary to heat up and let down very slowly, and keep dry before use. They should always be set in their own cementing material.

THE PRACTICAL TESTING OF REFRACTORY MATERIAL.

It will be gathered from the foregoing that, if examined in a proper manner, much information can be obtained by an intelligent study of

chemical analyses. These should be combined with experimental investigation, and fairly accurate results on a working scale may then be looked for. Practical tests, conducted so as to approximate if possible to working conditions, are strongly recommended. Fully reliable information as to the refractory qualities of material can only be obtained by continuous testing at high temperatures under working conditions; and extensive purchase of new material, of which little is known, should not be undertaken unless a few of the bricks have been tried for at least one season in the cross walls of a retort-setting or some such situation. For preliminary, and also comparative, tests, at time of settlement of contracts, some kind of testing furnace is desirable.

A very simple and easily managed coal-gas testing furnace, very well adapted for such work, is used by Dr. Davidson, D.Sc., the Chief Chemist of the Birmingham Gas Department (Fig. 9). A supply of coal gas is taken from the inlet of the holders (pressure about 6 to 7 in.), and a blast pressure

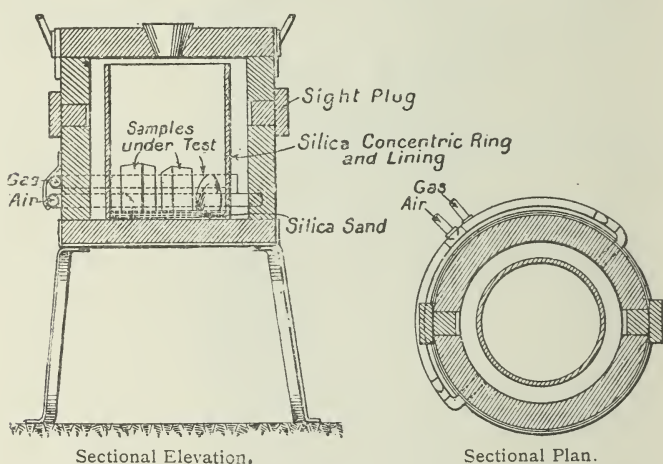


FIG. 9.—A Coal-gas Furnace for Brick-testing.

of 2 lb. is used. A temperature of $2,700^{\circ}$ Fahr. is readily obtainable, and on heating the gas and air, by passing the supply pipes through a combustion furnace, a temperature of $3,000^{\circ}$ Fahr. is possible. The gas burns in the annular space between the silica lining and the concentric silica tube, and the temperature of the furnace may be taken by means of a F ry pyrometer. This exceedingly simple instrument was fully described by Mr. John Bond in his paper on "Pyrometers," read before the Institution in June 1905. Seger cones may also be used for determining temperatures.

As more nearly approaching to the conditions of a working test, however, the author prefers the use of a furnace of a modified Deville pattern (Fig. 10). This furnace is easily manipulated; and exceedingly high temperatures can be obtained. The fuel used is a good hard coke, broken to about 2 in. diameter. When this is not available retort carbon may be substituted. The casing is of $\frac{3}{16}$ wrought iron; and the furnace portion A is lined with magnesite 3 in. thick. B is a wrought iron plate with four concentric rings of $\frac{1}{2}$ in. diameter holes, with a centre hole of 3 in. diameter. The chamber C is airtight, and contains a door and $1\frac{1}{4}$ -in. diameter connection for air-inlet, which is worked at about 2 in. water pressure. D is a magnesite

pedestal, fitted into a large centre hole F, and used for carrying the sample to be tested. A fire is lighted by means of wood and charcoal in the annular space, and afterwards coke is used, the blast being gradually increased. The air rises through the small $\frac{1}{2}$ -in. holes into the combustion chamber

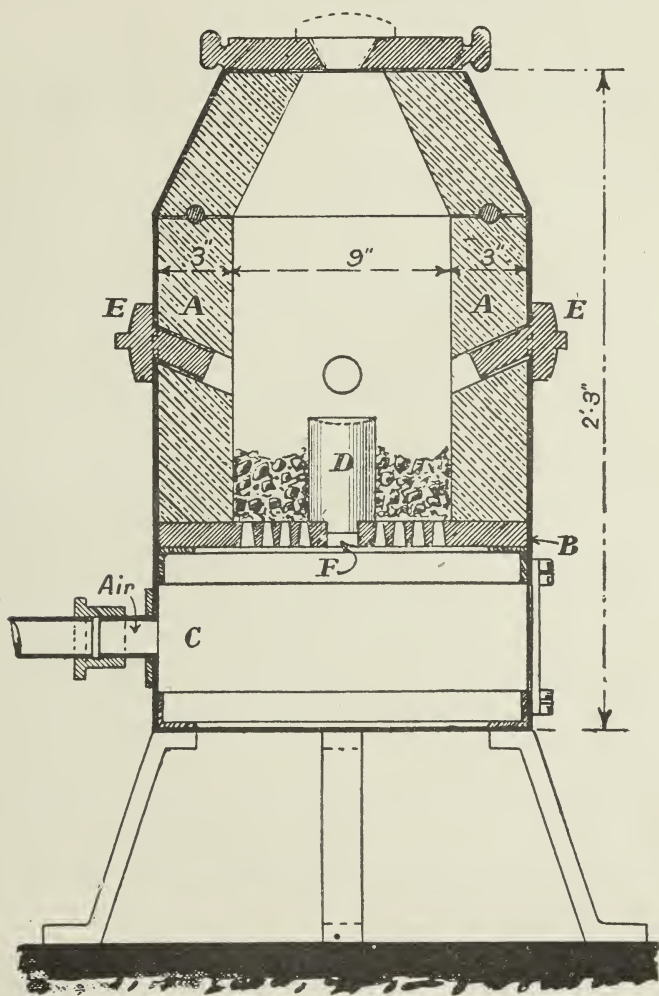


FIG. 10.—Testing Furnace using Coke Fuel.

above. After the completion of the test, the ashes may be removed through the large centre hole F. There are four sight-holes E, for taking temperatures (by means of the Férý pyrometer) and for adding fuel.

THE DESIGN AND SELECTION OF REFRACTORY MATERIAL.

This matter is, of course, a most important one ; and many instances might be given of failures in retort-settings due to the choice of unsuitable material or design.

All classes of refractory goods should be made of moderate size ; large blocks and tiles being eschewed. This particularly applies to quartz silica, and highly silicious clay material, which is unsuitable for large tiles and bricks where tenacity and toughness are desirable. For the lining of producers, good quality firebricks are most desirable. Silica bricks are quite unnecessary as regards temperature and also, by reason of the dust and impurities of the furnace gases, unscientific. The texture of the firebrick material used at these points should not be too open, but rather of heavy specific gravity, somewhat close and tough, with a low percentage of fluxes and free silica. These remarks also apply to the lining of carburetted water-gas generators.

To withstand the high temperature of combustion chambers, the author has found nothing so suitable as silica bricks of the Dinas or black ganister quartz type. Such bricks stand exceedingly well a combustion chamber temperature of about 2,500° Fahr., and show no signs of fusion after considerable wear, unless subjected to a cutting heat, in which case the iron-laden dust from the producer gas may cause fusion. Care should also be taken that the bricks used in the cross walls higher up in the setting are of sufficient refractoriness to withstand the working temperature, as drippings resulting from the fusion, or partial fusion, of these often cause trouble. If silica material is used in arch blocks or bed tiles for retorts, etc., they should be not larger, if possible, than about 18 in. long by 9 in. by 4 in. In the cross walls of the setting beyond the height of the combustion chamber, high-class fire-clay bricks of Glenboig, ganister, "best" Stourbridge, or Yorkshire, and Derbyshire "biscuit" silica, are quite suitable and desirable. Any of these may also be used in combustion chambers where moderate heats are maintained, with quite satisfactory results. Recently "artificial" silica bricks—i.e. fire-clay bricks to which an addition of 15 to 20 per cent. quartz, as sand or crushed rock, has been added—have been put upon the market. But these are generally unreliable, and their use is not desirable for high temperatures, at which they show considerable fusion. There is no doubt that in some cases the refractoriness of a dense clay free from fluxing bases is improved by the addition of quartz silica ; but these products should be used with great caution.

An average sample of retort-setting flue dust examined contained 48 per cent. of iron, and it will therefore be seen how important it is that all material subjected to its action should be of sufficient refractoriness to withstand the temporary rises in temperature which frequently occur in retort-settings, or the softening which will result therefrom will develop into complete fusion.

For retorts, the material used should be of the best. Owing to the variation of temperature, the grain should be as coarse and open as is compatible with toughness and tenacity. The author prefers segmental retorts to moulded ones, and the majority of the retorts at the Saltley Gas Works are of this kind.

The average life of moulded retorts of ordinary fire-clay material, taken over a large number of years, has been found to be from 700 to 800 days, and that of segmental retorts 1,400 to 1,600 days with gaseous firing and high heats. For inclined retorts, this latter figure is somewhat less. But for inclined and horizontal retort-settings the use of segmental retorts, although heavier in initial cost, results in a saving of more than 1d. per ton of coal carbonized during their life, taking account of all charges, labour, and materials. It may be urged that segmental retorts involve loss of gas owing to leakage ; but this is not found to be so. Such retorts, more-

over, take up expansion and contraction more readily and are more easily repaired.

In the case of moulded retorts, "hand-made" are to be preferred to those made by machinery. From the fact that the latter are made in one operation, it might be inferred that greater uniformity of composition is ensured than when the retort is made in "lifts" of about 15 in. at a time. This latter process, however, although having disadvantages, allows of several weeks' more tempering and slowly drying, which tend to lengthen the life of the retort. Moreover, the heavy pressure requisite for the manufacture of machine-made retorts causes the texture to be too close and compact; and the very nature of the process of manufacture forbids a coarse-grained material, which is very desirable. No comparative figures can be presented; but it is certain that machine-made retorts are rarely so satisfactory as hand-made ones.

Complaint is sometimes made that research is urgently required as to the relative conductivity of the various refractory materials for retort construction, and which is the best physical condition in which the material can appear. This may well be; but if, as seems probable, the conductivity varies as the silica content, there is a danger of a tendency to produce friable material lacking strength and altogether unsuitable in other respects. What is really first and most urgently needed is a retort which will give a "life" of 2,000 to 2,500 days, moderate in price and readily obtained.

For segmental retorts, the use of either (1) best Stourbridge, or Yorkshire Old Mine clay, with a mixture of 10 to 15 per cent. of "Pot" clay, and from 20 to 25 per cent. of burnt material, or (2) ganister material, or (3) Glenboig, give very good results; and although only costing about 10 to 15 per cent. more than those of ordinary fire-clay material, retorts so made have a much longer life. If these materials are not used throughout, they can with advantage be employed in the crown bricks of the retorts.

Hand-made bricks are usually to be preferred to machine-made ones on account of the dense, close structure associated with the latter. It is possible, however, by a judicious mixture of calcined material, and by coarse grinding, etc., to ensure a fairly open texture with pressed, machine-made bricks, and considerable quantities of such bricks have been used with satisfactory results. In the case of wire-cut bricks, in order to ensure a good "arris," the texture and grain must be fine, and therefore dense close-grain bricks result, which do not answer so well, frequently splitting, cracking, or fusing.

Finally, all classes of fire-clay goods, especially retorts and large blocks, etc., should be allowed plenty of time for making, tempering, and thoroughly drying in the sheds, whereby their life is perceptibly prolonged. Material which has been "rushed" rarely gives entire satisfaction. If large blocks are not dried slowly and thoroughly, a black core results, which will almost certainly cause trouble by shrinkage; and if this be not of great importance, it should be noted that if through the burning away of the outside portions the dark core be ever subjected to action of producer or other gases, it will melt out very easily.

Such cores also occasionally occur in large blocks, etc., due to insufficient burning and non-destruction of carbonaceous matter.

CONCLUSIONS.

A large number of typical specimens of refractory material have been examined and tested while preparing this Paper. It has been thought well not to publish the results of these tests beyond the statements already made;

but the most interesting of the samples, with details affixed, are produced for the inspection of members. One sample, however, is of considerable interest—i.e. the piece of retort material which has been in stock ten years and exposed to all weathers. This was carefully dried and slowly raised to a white heat, along with a piece of high-class Belgian retort material of good reputation, with the result that it withstood the test the better of the two. It would therefore appear that the exposure to weather has no serious effect on the refractory properties of firebrick material, and this is in agreement with the author's experience. Heats should, however, be raised very slowly in such cases. Silica goods should not be exposed to the weather.

It will be seen from the tests that good quality British fire-clay material will withstand moderately high temperatures (2,500° Fahr.) very fairly, and that between the best goods from the various chief sources of supply there is not great difference. At higher temperatures, however, they are not so refractory as some of the German samples tested. From a commercial and sentimental point of view this is perhaps regrettable. The highly refractory nature of these is no doubt due to the scientific investigation the German manufacturers have brought to bear on the raw material at their disposal. Their research methods compare remarkably with those employed by our manufacturers, for most of the large works have a highly trained scientific staff.

Time was when considerable quantities of retort material were shipped to the Continent from this country; but very little of this is now done, and the reverse operation has commenced. Compared with the 700 to 800 days which have been mentioned as the average life of moulded retorts of ordinary English fire-clay material working at high heats, some retorts of German make have been known to work in this country much more than double that period. This being the case, it is useless to still pursue the policy of *laissez faire*. The temperature of carbonization seems likely to rise rather than fall, and the advent of the vertical retort has made improvement in British retort material imperative unless business is to be resigned to foreign makers. There are large deposits of excellent fire-clay suitable for the manufacture of the highest grade retort material still unmined, especially in the Stourbridge, South Yorkshire, and Glenboig districts; and only thorough and scientific investigation and treatment are required to restore British fire-clays to their former pre-eminence. The annual cost of refractory material per ton of coal carbonized in gasworks usually ranges from 4d. per ton in the case of direct-fired, to 10d. in gaseous-fired settings. Having regard, therefore, to the huge expenditure involved and the issues at stake in our own industry alone, it would appear that joint action with manufacturers would be most useful. Consideration might well be given to the endowment of a research laboratory at the recently founded section of Gas Engineering at Leeds University, to which firebrick manufacturers would doubtless subscribe liberally.

NOTES ON THE COMPOSITION OF CLAY AND ON SILICA BRICKS.

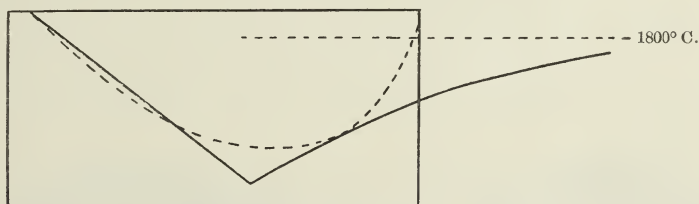
The following communication, dated November 18, 1916, was received by the President from **Professor H. Le Chatelier** (Paris):—

I am much obliged to you for sending me the address you delivered at the opening of the discussion of refractory materials. I have read it with great interest. Likewise the other communications which I received a few days later.

I take the liberty of drawing your attention to several points upon which I should like to express an opinion.

According to Mr. Bywater, whose paper is to be reprinted in the present symposium, clay is a mixture of true clay, quartz, and feldspath. This is not correct as to feldspath, which is practically never present in clays. All potash is there in the state of mica ($2\text{SiO}_3 \text{ Al}_2\text{O}_3 \frac{1}{3} \text{ K}_2\text{O} \frac{2}{3} \text{ H}_2\text{O}$), as Mr. Vogt showed long ago.* It is the conclusion of a 200 page report on clays. Moreover, Mr. Bywater's analysis fully confirms this assertion, for he found that nearly all the potash is soluble in sulphuric acid, which would not be the case with potash originating from feldspath.

The curve of fusibility of the mixtures of silica and alumina given by Mr. Bywater requires some modification, because the extrapolation would lead to an infinite temperature for the fusion of the quartz. The curve is bound to have the form shown in heavy lines on the sketch.



Molecules SO_2 for one Al_2O_3 .

(Pure silica corresponds to an infinite number of SiO_2 molecules for one Al_2O_3 .)

The conclusion that a chemical analysis cannot enable one to foresee the fusibility of a clay is perhaps true to a certain extent, but the analyses given in support of this assertion by Mr. Bywater (*supra* p. 38) do not seem to be borne out by the facts. They contain no indication of alkalis, whereas there is no clay without alkalis. Their presence is very difficult to determine by chemical analysis, and yet they have the greatest influence on the fusibility. It is true, however, that on rapid heating there might be a momentary partial fusion which would cease when the combinations have reached their stable state. Let us take feldspath for example. It only begins to soften between $1,100^\circ$ and $1,200^\circ$. Let us compare a mixture of silica, alumina, and carbonate of soda, having exactly the same composition. Semi-fusion will be noticed at about 800° , at the melting-point of carbonate of soda. But the soda will gradually combine with silica and the alumina, and in a short time the mixture will assume the properties of real feldspath. The differences of fusibility with identical compositions are essentially transitory. They are seen during the first burning of bricks, but not in their subsequent use.

* *Contribution to the Study of Clays and Ceramics*, published under the auspices of the Société d'Encouragement, p. 193, Dunod.

In his paper, Mr. Bywater indicates on p. 39 that alumina is only slightly more refractory than silica. With this I do not agree. There is a very great difference between the melting-points of these two bodies, namely from 200° to 250°. Silica melts at about 1,800° and alumina at about 2,050°. Nor does it seem correct to say that the mixture corresponding to kaolin is the most refractory of them all. The fusibility is considerably diminished by additions of alumina; it decreases gradually from the mixture 15 SiO₂, Al₂O₃, which melts at 1,650°, to pure alumina at 2,050°. Pure kaolin melts at about 1,800°, like silica.

I thought the Faraday Society might like to have these observations, and I take the opportunity of saying that in making the above comments I have at the same time found a considerable amount of interesting information in this work.

In a few days I will send you a series of photographs taken on silica bricks and on quartz used in the manufacturing of them.

I send you herewith, as an example, a photograph of a silica brick used for a very long time in a steel furnace. The photograph (Fig. 10) was taken in polarized light: magnification 200 diameters. The brick is completely transformed into tridymite, a variety of silica with a density of 2.28.

Data.—One of the great difficulties I meet with in studying refractory materials is the impossibility of obtaining from works engineers an exact description of the defects shown by refractory products. I am told "the furnace must hold," but one cannot build a Siemens furnace for a test.

For silica bricks I have at present two indications. I have seen furnaces where the silica brick gradually scales off from the hot surface and ends by completely falling to pieces. Further, I am informed by steelworks engineers that most frequently the roofs are destroyed by fusion, following on projections of cinder which melt the surface of the silica bricks. One can observe stalactites running little by little from the roof, which gradually diminishes in thickness.

In your address, p. 12, you say that the principal defect of silica bricks is that of being "half bakes." These bricks would fuse as easily as clay bricks. What form does this fusion take? Does the brick run drop by drop, or does it simply disintegrate? What exactly is the phenomenon observed apart from any explanatory theory? Are there any other causes of destruction? Is there no sign of the expansion inevitable with insufficiently baked bricks? In cement kilns I have seen a silica brick roof rise so much that the kiln was destroyed in consequence.

Appendix dated November 19, 1916: Here are the photographs I mentioned in my letter yesterday. Among the photographs of quartzites, that of Souvigny quartz (Fig. 1) represents one of the materials considered to be the best in France for manufacturing silica bricks. It is a very fine grain quartzite.

The specimens photographed by natural light are reproductions of test bricks made in the laboratory by very rapid baking at a very high temperature. In their filling one can see differently shaped crystals of one and the same variety of silica of low density; it is cristobalite. These crystals do not exist in bricks burned in the trade; that is, very slowly. This variety of silica tends to change gradually into tridymite; but its crystals are very fine and difficult to recognize in most cases. Nevertheless they are clearly visible in the "Star" brick (Fig. 9) of American origin, which must have been baked for a particularly long time. In the baking which bricks undergo on manufacture, the crystals of tridymite never assume the dimensions and extent seen in bricks which have been long in use in steel furnaces, like the one of which I sent you a photograph in my last letter (Fig. 10).

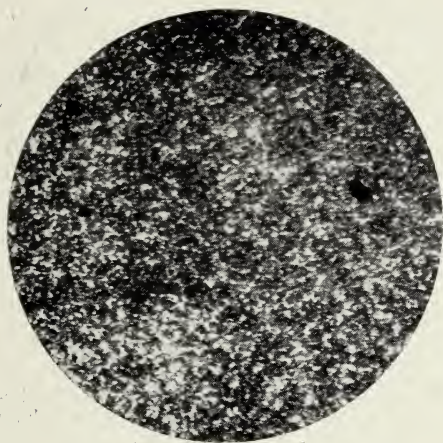


FIG. 1.—Quartzite from Souvigny (Allier).
Polarized Light : 200 diams.

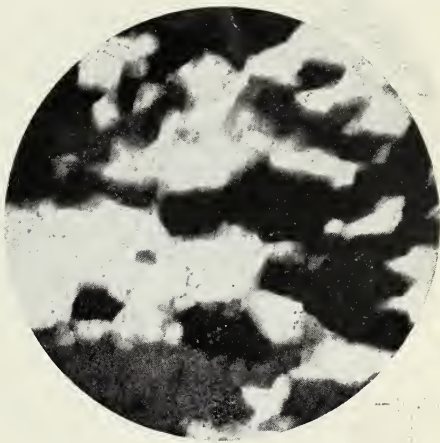


FIG. 2.—Quartzite from Bouchard.
Polarized Light : 200 diams.

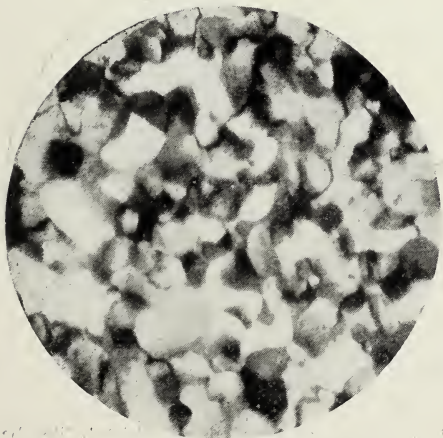


FIG. 3.—Quartzite from St. Fortunat.
Polarized Light : 200 diams.

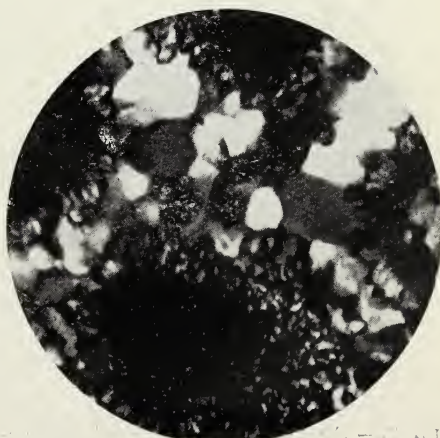


FIG. 4.—Quartzite from Messargès (Allier).
Polarized Light : 200 diams.

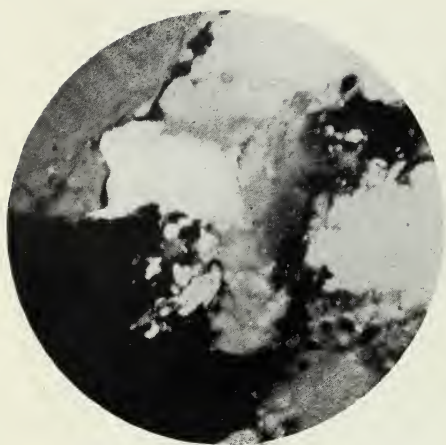


FIG. 5.—Ardèche Quartzite. Stips of Mica between the grains of Quartz. Too fusible for use.

Polarized Light : 200 diams.

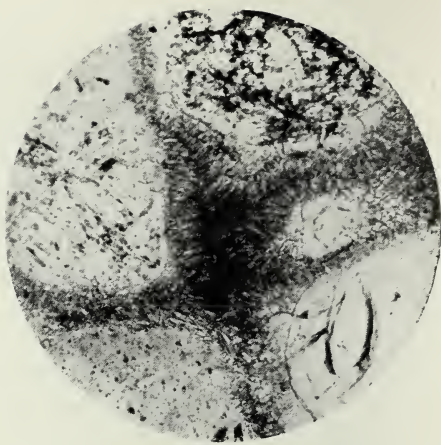


FIG. 6. — Crystallization of Cristobalite between the grains of Quartz after baking at 1,700° C. Limestone flux.

Natural Light : 200 diams.



FIG. 7. — Crystallization of Cristobalite between the grains of Quartz after baking at 1,700° C. Fluor flux.

Natural Light : 200 diams.



FIG. 8. — Crystallization of Cristobalite between the grains of Quartz after baking at 1,700° C. Ferruginous flux.

Natural Light : 200 diams.



FIG. 9.—“Star” brick. Two fragments of Quartz not transformed. Crystals of Tridymite in the filling.

Polarized Light : 200 diams.



FIG. 10.—Assailly Brick from flue of a steel furnace. Silica transformed into Tridymite.

200 diams.

THE TEXTURE OF FIREBRICKS.

Dr. J. W. Mellor (Stoke-on-Trent) read the opening Paper of the symposium, dealing with "The Texture of Firebricks."

What constitutes a good firebrick? is a favourite question, and one which does not admit of a satisfactory answer. If the question be put to any particular manufacturer, it would be human nature if he were guided in his answer by the character of his own products; and if the user, likewise, were guided in his answer by his own particular needs. The requirements from firebricks vary so widely in different furnaces, or in particular parts of a single furnace, that the ideal firebrick can be defined only in abstract terms, and this the more because some properties of firebricks are antagonistic in the sense that some characteristics can be highly developed only at the expense of others. For example, resistance to crushing strains and to abrupt changes of temperature are antagonistic in that usually the one can be accentuated only at the expense of the other.

The manufacturer who seeks to develop particular qualities in his bricks, especially fitted for particular purposes, is often handicapped by competition against bricks made possibly with good refractory clays, but in which no attempt has been made to control the product. This may appear to be unfair, but the injustice will prevail so long as the criteria of the quality of firebricks for specific purposes remain indeterminate. Probably some such idea prompted the Refractories Committee of the Gas Engineers in their pioneer attempt, so far as this country is concerned, to draw up a specification for refractory materials.

Texture is one of the most important qualities of a firebrick, since, assuming that the chemical composition and refractoriness are otherwise satisfactory, the life and character of the firebrick are largely determined by its texture. The texture of a refractory may vary from that of the light porous bodies used in making bricks for insulating boilers, etc., to non-porous or vitreous bodies used in making crucibles, acid-resisting bricks for acid towers, etc. There are a quite a number of intermediate types. I have followed the history of most of these types from the point of view of both the manufacturer and consumer, and although the subject gets more and more complex with increasing knowledge, a few broad principles are now available which I think it will be most profitable to review, in order that the variations in the texture of firebricks can be understood. This review may be of some assistance in deciding what is the best type of firebrick to stand against certain specified conditions.

The different textures are illustrated by the samples on the table. These bricks, etc., have been cut transversely, and an exposed face polished and photographed. A glass plate was then cemented on the polished faces by means of hot Canada balsam. This is a new and elegant method of illustrating the texture of bricks for which I am indebted to Mr. Lomax. Fig. 1 represents the type of a British refractory from fire-clay materials, Fig. 2 represents a

piece from one of the most famous German factories, Fig. 3 represents a piece from a fire-clay brick strongly fortified with coarse-grained silica, Fig. 4 represents the texture of a peculiar type of firebrick made from what corresponds with china-clay rock, but rather less pure. In the Lee Moor firebrick the siliceous and micaceous residues are worked up after the removal of china clay; in Fig. 4 the whole of the china-clay rock is treated. This brick is particularly interesting, for the materials have been mixed by Nature, and she has made a good job of it. Figs. 5 and 6 represent two types of silica brick. Fig. 5 represents a crushed ganister brick, and Fig. 7 the sandy Ewell brick. Figs. 8 and 9 are acid-resisting bricks for Glover's towers and the like. They are coarse-grained and more or less vitreous. Fig. 10 represents a light porous brick. Fig. 11 represents a piece of glass-pot after heating three months.

The more important mineral constituents of clays are the granular elspathic or micaceous fluxes, granules of clay proper, and quartz grains. Virtually all fire-clays may be considered to have been made by Nature by mixing these three components—the *primary constituents*—with what might be called the *secondary constituents*, or the accidental—often deleterious—impurities: schorl, pyrites, siderite, etc. The osmose process of clay purification is one means of removing the deleterious accidental impurities from clays, but before proceeding to that elaboration, slipping and lawning the weathered clay should be tried. The latter can be made to do much of the work claimed as the peculiar merit of the osmose process. Either process of preparation considerably improves most fire-clays, but of course it simultaneously runs up the cost. It is, however, a question of arithmetic and trial whether the additional labour is worth while in any particular case.

When the clay is burnt in the kilns, the fluxes begin to melt at about 900° or $1,000^{\circ}$, and they begin to attack the surfaces of the clays and quartz grains. At a still higher temperature the granules of clay and quartz which are in contact also begin to react, so that clay is a high temperature flux for quartz (or silica), and quartz (or silica) is a high temperature flux for clay.* With silica and ganister bricks, either clay or lime, or both, are the fluxes. The fluxing action, of course, is necessary to bind the brick into a compact whole, to give the brick a high crushing and tensile strength, and to give the brick the power of resisting abrasion and attack by flue-dust, slags, etc. This fluxing or vitrification is a time reaction—it is relatively slow at low temperatures and fast at high temperatures; a long protracted fire at a low temperature can produce virtually the same contraction as a shorter fire at a higher temperature. There are, of course, slight differences due to secondary effects.†

The Size of Grain.

There is an enormous increase in the number of granules for a given mass of clay as the dimensions of the particles are reduced. If the grains of a clay were all a millimetre in diameter there would be, in round numbers, 720 grains per gram, and if the grains were 0.0001 mm. in diameter, the number would increase to the enormous total of 720,000,000,000,000 grains per gram. Of course, clay grains are not spherical, and they are not all the same size, but there are methods of grading the granules approximately into groups with certain assigned average diameters. The hypothetical case will, however, best illustrate my meaning. Similar remarks also apply to the increase in the number of points of contact of the granules as their diameter is

* H. A. Seger, *Tonind. Ztg.*, **17**, 391, 1893; *Gesammelte Schriften*, Berlin, 445, 1908; Amer. trans., Easton, **1**, 545, 1902; B. Neumann, *Stahl und Eisen*, **30**, 1505, 1910; O. Boudonard, *Journ. Iron Steel Inst.*, **67**, i, 339, 1905; G. Stein, *Zeit. anorg. Chem.*, **55**, 159, 1907; E. S. Shepherd and J. A. Rankin, *Amer. Journ. Science* (4), **28**, 301, 1909.

† J. W. Mellor, *Trans. Eng. Cer. Soc.*, **9**, 79, 1910; *Collected Papers from the County Pottery Laboratory, Staffordshire*, London, **1**, 106, 379, 1914.

diminished. Reducing the diameter of the grains from 1 to 0.0001 mm. diameter raises the number of points of contact of the grains from, say, 2,160 to 2,160,000,000,000,000, because the number of points of contact n of a group of spheres varies inversely as the cube of their radius r such that $nr^3 =$ a constant. Consequently, if the vitrification of a clay is the result of a reaction between the surfaces of contact of the granules, the speed of vitrification must increase according to a similar law when the area of the surfaces in contact with one another is augmented. This conclusion is in agreement with some observations made some years ago on the effect of increasing fineness of grain on the fire contraction of clay bodies.

It follows also that pressure might be expected to lower the softening temperature of a clay* by bringing the surfaces of the granules into more intimate contact. Observations on this phenomenon have showed that with clays of approximately the same† grain-size, the softening temperature is reduced by pressure‡ in accord with the exponential law, Ce^{-kP} , where C denotes the squatting temperature of the clay under no load, P denotes the pressure in lb. per square inch, and k is a constant of the order 0.001, but which has in general smaller values for siliceous than for aluminous clays. The evidence for this relation was recently published, and more extended observations are in progress.

There is a valuable lesson in this discussion. Anything which favours the vitrification of a clay reduces its refractoriness or fire-resisting qualities. Consequently, other things being equal, the coarser the grain of a clay the higher its softening temperature, and the coarser the texture, the more refractory the brick.‡ This is very noticeable with high-temperature fluxes like mixtures of clay and fine-grained quartz, where the temperature of vitrification may be so reduced that the admixture spoils the firebrick. On the contrary, if the quartzose silica be coarse-grained, the refractoriness may appear to be improved. Firebricks made with some clays, with or without fine-grained silica, break down at temperatures which they withstand when made from the same clay mixed with coarse-grained quartz. This is the case, for example, with sample Fig. 3, which otherwise is not a particularly well made brick. Compare also samples Figs. 5, 6, and 7, which are not very different in composition, but one has some coarse-grained quartzose silica, which augments its refractoriness quite appreciably.

There is a precaution: the quartz grains should be angular, and not in the form of rounded pebbles. The reason for this will be apparent on comparing sections of bricks made with the two forms of grog—angular and rounded grains. The angular grains (samples Figs. 2 and 4) are firmly embedded in the clay matrix, while the rounded grains (samples Figs. 1 and 3) are loosely held by the clay bind and are easily picked out. Again, angular fragments pack together more closely with the clay and form a more compact skeleton for the brick than rounded grains—in illustration, contrast the samples represented by Figs. 2 and 3.

This has no reference to the mere packing of masses of different sized grains of the same kind. The packing of grains of an irregular shape and size has not been investigated by mathematicians to anything like

* J. W. Mellor, A. Latimer, and A. D. Holdcroft, *Trans. Eng. Cer. Soc.*, **9**, 126, 1909; *Collected Papers*, **1**, 247, 1914.

† J. W. Mellor and B. J. Moore, *Trans. Eng. Cer. Soc.*, **15**, 117, 1916.

‡ H. O. Hofman and B. Stoughton, *Trans. Amer. Inst. Min. Eng.*, **28**, 440, 1898; H. Ries, *ibid.*, **34**, 205, 1904; H. O. Hofman, *ibid.*, **34**, 956, 1904; R. F. Weber, *ibid.*, **35**, 637, 1905; F. Kraze, *Tonind. Ztg.*, **32**, 934, 1908; J. W. Mellor, *Trans. Eng. Cer. Soc.*, **9**, 79, 1910; *Collected Papers*, **1**, 106, 1914.

the same extent as the packing of spherical grains. F. H. King* found that—

The pore space of sands with angular grains is much larger than it is with rounded sands of the same sizes of grains, and in the case of crushed glass, whose grains are much more angular than those of crushed limestone, which have a tendency to be cuboidal in form, the pore space is largest of all.

This question is not of mere academical interest, since the explanation of the grain (not exactly the texture) of clay will probably turn on the mode of packing of its constituent granules. I prepared a note on this subject about three years ago, before the war, but left it unpublished until I could see a way to test some ideas experimentally. When a slab is cut from the clay as it leaves the pug, moulded into a circular disc, and fired, an elliptical, not a circular disc is sometimes obtained. Again, fast dried or fast fired bricks are larger than slowly fired bricks. These and kindred phenomena are no doubt dependent on the grain of the clay.

There is another important point to remember. When clays are heated on a gradually rising temperature the surfaces of the more fusible granules melt first. Hence again, quite independently of the action of the fluxes, a fine-grained clay with its augmented internal surface will vitrify faster and at a lower temperature than a coarser grained clay of the same composition. There is therefore a cumulative action in favour of coarse-grainedness for highly refractory bricks.

After-contraction and After-expansion.

The changes which occur during the firing of refractory materials belong to a class which I called some years ago *arrested reactions*.† In these the chemical or physical changes are arrested at particular and definite stages before they are completed. When firebricks are burned or fired in the kilns, the fluxes melt and dissolve the less fusible materials binding the whole more or less firmly together. A certain amount of contraction occurs during this operation, and if not completed during the firing of the brick, it will subsequently continue when the brick is in use. I have elsewhere called this secondary effect the *after-contraction* of the brick,‡ to distinguish it from the primary contraction or fire shrinkage which occurs when the bricks are burned. If the after-contraction is considerable, the masonry of the furnace will most certainly be displaced when the bricks are in use. The after-contraction should be small, certainly less than 1 per cent. A few years ago, 2 to 3 per cent. after-contraction was common.

The contraction test of the gas engineer's specification was an attempt to deal with the after-contraction of firebricks, and it served a useful purpose in emphasizing the importance of adequate burning. As soon as the firebrick manufacturers realized what the consumer wanted, they gained control of the difficulty, and the after-contraction of commercial samples was reduced from about 1 to about $\frac{1}{2}$ per cent. in a comparatively short time. It is probable that many more difficulties would soon be solved if the consumer would give the manufacturer a clear idea of what is wanted. Inspiring talk about "improved firebricks," "scientifically made firebricks," or "superior German firebricks" is usually playing with words à la *journaliste*, since it is too vague to have any definite meaning.

* F. H. King, *Ann. Rep. U.S. Geol. Sur.*, 19, ii., 205, 1899.

† A. Heath and J. W. Mellor, *Trans. Eng. Cer. Soc.*, 7, 80, 1907; *Collected Papers*, I, 138, 373, 1914.

‡ J. W. Mellor, *Collected Papers*, I, 307, 316, 1914.

It is usually impracticable to eliminate all the after-contraction when the firebrick is originally burned. If the brick were fired a dozen times, some after-contraction could still be detected, unless the brick had begun to disintegrate under a given set of conditions. The magnitude of the after-contraction with more burning seems to diminish according to an exponential law, or law of geometrical progression. The object of the firebrick manufacturer is to make the after-contraction negligibly small. After some years' experience with the contraction test devised for firebricks by gas engineers, I have come to the conclusion that it is one of the most useful tests, since it generally makes the weakness of poor bricks apparent by mere inspection. It would probably be still more useful in this respect if it were made a little more severe.

With silica firebricks there is usually an *after-expansion*, not contraction. This is due to the gradual change of quartzose silica with a specific gravity 2.65 to another different kind of silica with a specific gravity 2.3. The complete change thus involves a 16 per cent. expansion; it is a slow reaction and usually progresses a little each time the brick is fired. Quartzose silica also occurs in clays, and when the clays are heated the quartz expands in a similar manner, unless it be dissolved by the fluxes. The fluxes in a clay also expand about 6 per cent. in firing, so that the normal contraction of a firebrick is the joint effect of an expansion of the quartz and fluxes, and about a 4 per cent. contraction which clay normally undergoes when fired, whereby its specific gravity changes from 2.6 to 2.7; the particles are also pulled closer together by the surface tension of the molten fluxes. The joint contraction of the components of a fire-clay brick is far greater in magnitude than the expansion, so that the resultant effect is a contraction; the converse of this applies with silica bricks, where the resultant effect is an expansion.*

In the early days of the application of the gas engineer's specification, manufacturers of firebricks with a large after-contraction sometimes mixed the materials with enough siliceous material to make the brick give a good result with the contraction test, even with underfired bricks. In some cases the two opposing changes were perfectly balanced, and the resultant change in volume was zero. Naturally, this method of satisfying the test was condemned as a cheat, but I see no particular harm in the addition for many purposes, provided the composite brick be well fired, the added silica be coarse-grained, and the binding clay is suitable.

Grog.

The study of the action of grog in firebricks is most interesting, and is rather complex. In the ordinary course of things grog may be regarded as burnt fire-clay (or ground firebrick), which is mixed with the fire-clay to serve as a skeleton to facilitate the drying, to control the contraction during the drying and firing of the clay, and also to modify the behaviour of the refractory material when in use. The meaning of the term "grog" is also extended to include non-plastic materials other than burnt fire-clay.

Here we are only concerned with the effect of the grog on the properties of the finished brick. When grog is specially made by burning the fire-clay from which the bricks are manufactured, the main difference between the grog and the rest of the brick turns on the fact that the grog has been fired twice and the remainder of the brick has been fired but once. The grog

* J. W. Mellor, *Trans. Eng. Cer. Soc.*, 5, 75, 1906; *Collected Papers*, I, 19, 1914; J. W. Mellor and A. D. Holdcroft, *ibid.*, I, 272, 1914; *Trans. Eng. Cer. Soc.*, 9, 94, 1911.

then behaves as an independent constituent, and is fixed in the brick by the fluxes of the surrounding clay. The difference in the nature of the grog and the rest of the brick becomes less and less every time the brick is afterwards fired, so that after such a firebrick has been in use at a high temperature for some time, the grog is indistinguishable from the rest of the brick. This is illustrated by Figs. 12 to 14. Fig. 12 represents a slice of the unfired body; Fig. 13, the body fired to about $1,100^{\circ}$; and Fig. 14, the same body fired to $1,350^{\circ}$. All these bodies are magnified about 50 diameters. In Fig. 14 the difference between the grog and binding clay is becoming less pronounced. If the grog has been prepared at a much higher temperature than the brick is afterwards fired, or if the grog is made from firebricks which have been in use for some time, the grog retains its distinctive character for a longer period. I have followed the life-history of grog through forty firings, each extending over about six days up to cone 10; after such a treatment I could not detect any difference microscopically between the grog and the bond clay. Curiously enough, the squatting temperature of the new brick is sometimes nearly 20° higher than that of the clay when the brick has been made by admixture with its own coarse-grained grog. This is a striking illustration of the importance of texture on the character of a firebrick. With proper control, the grog can retain its individuality at high temperatures, and also when the bricks are fired for long periods of time.*

I must here indicate a danger which is sometimes ignored. Great care may be taken in the grading of the grog (or the non-plastic material) added to a fire-clay, and it may be imagined that the manufactured product was made with grog of a specified size. The clay and grog, however, may be afterwards mixed on a revolving pan with heavy rollers, which naturally have a tendency to reduce the size of the grog. The grinding of the mixture of clay and grog under such conditions undoes the careful work involved in the grading of the grog. Therefore, the clay and grog should not be mixed in any form of machine which exerts a grinding action, assuming, of course, that the manufacturer desires to have control of the texture and composition of the finished product. The grog and binding clay should be suited to one another, so that the grog and clay are knit together into a compact mass when the bricks are fired. If otherwise, the broken surface of the finished material will appear as a crumbling mass with projecting pieces of grog. If the binding clay contracts too much during drying and firing—particularly if large pieces of grog are used—the binding clay will open into a series of cracks, and the crushing strength of the brick will be weakened. In that case the binding clay has to be mixed with dust grog or tempered with another less contractile clay.

The net result of this discussion is to show that conditions which bring the surface of the clay granules into more extended or into closer contact make clay soften at a lower temperature, and the problem of getting the maximum refractoriness from a given clay is virtually solved for normal furnace conditions. Of course, the refractoriness of a clay can be augmented still more by fortifying it with some of the higher refractories, shrunk bauxite, shrunk zirconia, carborundum, and the like.†

It is not always advisable to make firebricks satisfy the condition for maximum refractoriness at the expense of other properties. Bricks with the resulting coarse-grained texture acquire certain undesirable qualities. True enough, the more coarse-grained the texture, the less liable the refractory

* J. W. Mellor, *Journ. Soc. Chem. Ind.*, **26**, 375, 1907; *Collected Papers*, **1**, 43, 579, 1914; G. Rigg, *Mct. Chem. Eng.*, **8**, 523, 1910.

† *Vide* R. S. Hutton, *Trans. Eng. Cer. Soc.*, **5**, 110, 1906.

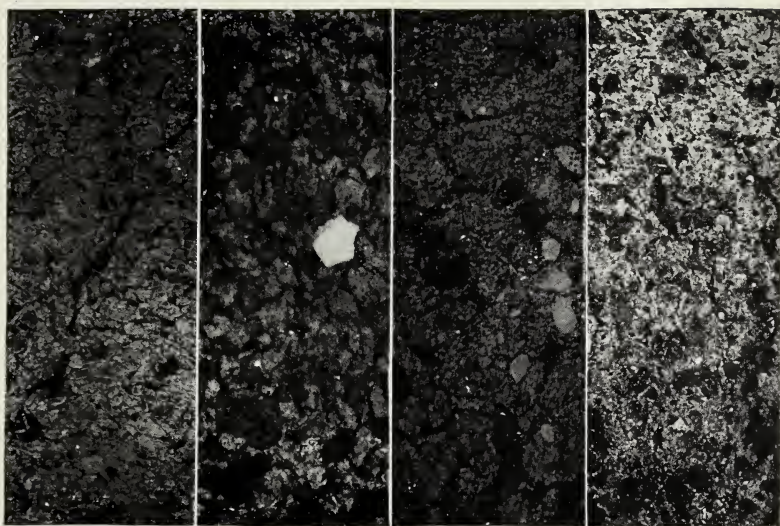


FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

All slightly reduced.

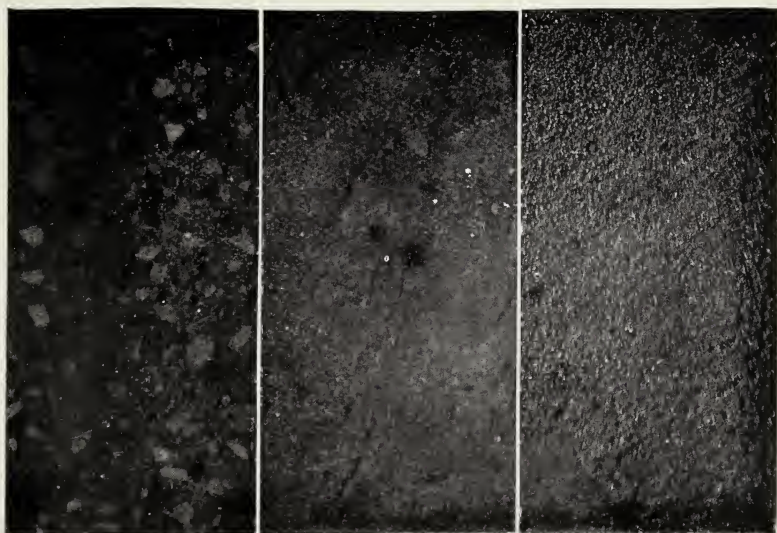


FIG. 5.

FIG. 6.

FIG. 7.

All slightly reduced.

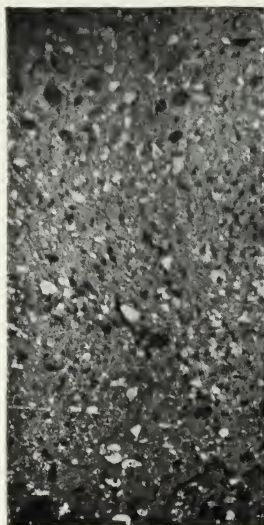


FIG. 8.



FIG. 9.

All slightly reduced.



FIG. 10.

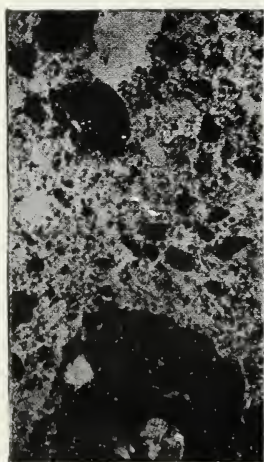


FIG. 12.

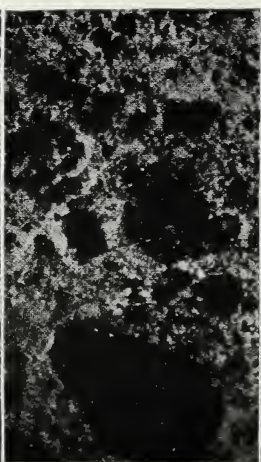


FIG. 13.

Magnification 50 diameters.

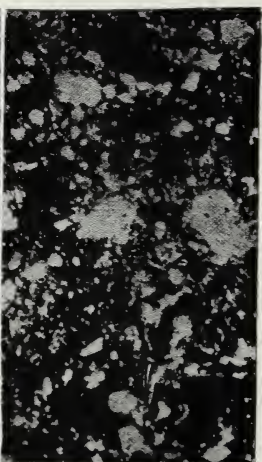


FIG. 14.

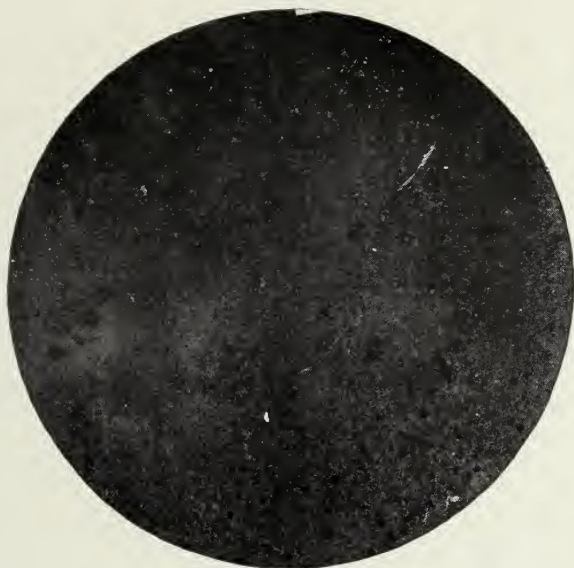


FIG. 11.
Slightly reduced.

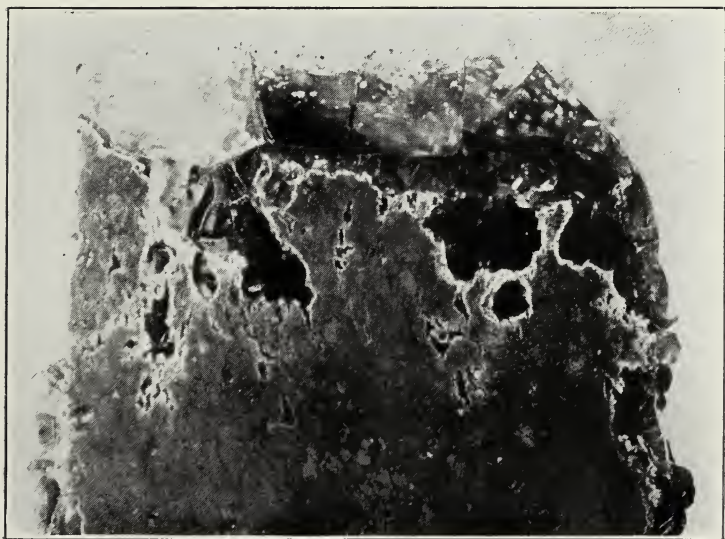


FIG 15.
Slightly reduced.

material to crack or split with abrupt change of temperature.* The porosity test of the Gas Engineers' specification was designed to draw attention to this property. It was based on the observed porosity of the most successful British and German retorts, and it appears to be a good guide to practical requirements. Unfortunately, in one or two cases, the specification appears to have been misunderstood, for it was argued that one cannot have too much of a good thing. As a result of this overzeal, some retorts were put on the market with an abnormally high porosity. The result was disastrous. It appears to have been forgotten that the manufacturer, here as in many other cases, has to balance opposing and antagonistic properties to suit his particular purpose. The crushing strength and tenacity of a coarse-grained refractory material are always low. The retorts had a very feeble tensile strength, they were very friable, and readily disintegrated with shocks, abrasion, etc. Coarse-grained bricks are also rapidly penetrated by flue dusts and slags. All these desirable qualities are improved by making the refractory material with a fine-grained texture. The maximum refractoriness and resistance to abrupt temperature changes may be far greater than what is wanted, and it may be desirable to sacrifice some refractoriness, etc., to enhance other qualities.

Machine v. Hand-made Firebricks.

There is often a strong prejudice against machine-made firebricks. It will be readily conceded that a badly made machine-brick is in all probability worse than a badly made hand-brick, but I am not prepared to say that if the necessary precautions are taken in the preparation of the clay as good a brick cannot be made by machinery as by hand. The subject is one which wants careful re-examination. I will try to show that the prejudice is probably the result of an unfair comparison. There is little doubt that when a weathered clay is allowed to stand in a moist condition, it becomes more and more plastic, and it then readily adapts itself to the mould. According to the testimony of old potters, when machinery was introduced for the preparation of the clay body for the manufacture of pottery, there were serious complaints about the low plasticity of the body. The clay was not so buttery and the percentage loss in cracked ware increased. As a result, it was said that machine-made bodies were not so good as hand-made bodies. There are several converging lines of evidence which show that the essential difference was not machinery *versus* hand, but rather depended on the difference in the time the clay was allowed to stand in contact with water.†

There is also a tendency for the machine-made body to be less uniform in texture. Pug-mills are not really good mixers. With pugs mixing, say, clay and grog, the eject from the pug has a tendency to be more or less laminated into patches poor and patches rich in grog. The preparation of the clay for hand and machine working usually differs in a way which materially affects its working properties and texture. Contrast, for instance, the texture of samples Figs. 1 and 2. The last named happens to be a German refractory; it is very well made and the texture is uniform. The texture of sample Fig. 1 is not so uniform; there are signs of lamination. If the texture of the brick be not uniform, it is highly probable that strains will set up when the brick is being heated, owing to a difference in the rates

* H. W. Edwards and A. Leese, *Trans. Eng. Cer. Soc.*, 2, 14, 1902.

† The qualities which depend upon the internal cohesion of a brick appear to be better with well-made machine bricks than they are with hand-made bricks. Cf. A. Hahn, *Ber. Ver. deut. Fab. feuerfester Prod.*, 33, 147, 1912; 34, 82, 1913.

of expansion of the different parts. This will lead to the formation of fissures and cracks, and, may be, also to spalling. A prime desideratum with machine or hand-made bricks is uniformity of texture. Other things being equal, that process of manufacture which is least liable to yield bricks with an irregular texture will give the best results. In the dry or semi-dry processes of machine-making, films of air between the granules prevent their packing together so well as in bricks made by plastic processes, and this again has a tendency to make machine-made bricks less sound than hand-made bricks. I mention these points, firstly, because they affect the texture of the brick, and secondly, because when we once recognize clearly the essential difference between machine and hand-made bricks, the difficulties with machine-made bricks will the sooner be overcome.

The texture of some varieties of natural rock is fairly uniform, but when large slabs are heated, they are very liable to split and crack under conditions where a similar material made artificially would remain intact. The trouble arises from the chemical and physical changes which occur in the material as the heat travels from the hotter to the colder sides; e.g. the gradual transformation of quartzose silica with a specific gravity 2.65 to a variety with a specific gravity about 2.30, involving a 16 per cent. expansion, must produce drastic changes in the internal structure of the material. In the present state of our industry, *I do not think I can overemphasize the importance of uniformity in texture, be it coarse or fine.*

Chemical Analysis.

I have been requested to speak about chemical analysis. It will be obvious that the chemical analysis gives no information about the grain or texture of a clay. As a result, the empirical methods of Bischof, Seger, and Ludwig* for estimating the refractoriness of a clay from the chemical analysis must all fail in particular cases, and this weakens our confidence in their prognostications. No satisfactory substitute for an actual determination of the refractoriness has yet been found. This fact has long been recognized, and the old argument *falsus in uno falsus in omnibus* is sometimes pushed to the absurd extreme. We must clearly distinguish between the three cases, coarse and fine grained fire-clays, and firebricks. Chemical analysis certainly gives an important clue to the chemical character of a clay, but the chemical analysis of a composite brick taken *en masse* would be misleading unless it were done for the purpose of checking the mixing and blending. In the case of a composite brick taken *en masse*, that is, of a brick fortified with quartz, carborundum, zirconia, bauxite, etc., the ideal thing is to indicate the approximate proportion and character of the fortifying agent and of the binding clay. The statement can be verified, if desired, by an analysis of the material in bulk. The information, of course, cannot be a trade secret, since if it were worth while the secret would be quickly revealed. Trade secrets flourished in the dark ages, and prevail most in works whose future lies furthest behind.

* E. Richters, *Journal. prakt. Chem.*, **104**, 191, 1868; *Untersuchungen über die Ursachen der Feuerbeständigkeit der Thone*, Breslau, 1868; *Dingler's Journ.*, **191**, 59, 150, 229, 1869; **197**, 268, 1870; C. Bischof, *ibid.*, **159**, 54, 1861; **161**, 208, 291, 1861; **164**, 116, 1862; **169**, 353, 455, 1863; **170**, 43, 1863; **194**, 420, 1869; **196**, 420, 525, 1870; **198**, 396, 1871; **200**, 110, 289, 1871; H. A. Seger, *Tonind. Ztg.*, **1**, 290, 1877; E. Cramer, *ibid.*, **19**, 632, 647, 1895; T. Ludwig, *ibid.*, **29**, 773, 1904; P. Jochum, *Zeit. Ver. dent. Ing.*, **39**, 53, 317, 1895; H. A. Wheeler, *Missouri Geol. Surv.*, **11**, 146, 1896; E. Kochs, *Zeit. angew. Chem.*, **19**, 2123, 1906; E. Kochs and F. Seyfert, *ibid.*, **16**, 14, 719, 1901; J. W. Mellor, *Journal. Soc. Chem. Ind.*, **26**, 375, 1907; *Collected Papers*, **1**, 43, 1914; G. W. Cronquist, *Sprech.*, **40**, 40, 1907.

Given the chemical composition of a brick, expressed in this form, it is possible to say whether it is likely to be chemically affected under the conditions which prevail in any given furnace. If the clay itself is coarse-grained, it should be separated into two or three fractions by levigation, and the chemical character of each portion determined by analysis. An example occurs with the sample Fig. 4.

Coarse-grained Firebricks.

The rule that coarse-grained firebricks usually resist sudden changes of temperature better than those of a closer texture is not without exceptions. We come across a clay every now and again which has the property of resisting abrupt changes of temperature even when made into refractories with a fine texture; and conversely, we encounter clays particularly liable to split and crack even when coarse-grained. I do not understand the difference. The couple of clays which I have met of the former type have been clays fairly high in alumina, and the latter are high in silica, but I am not yet prepared to elaborate this subject. I do know that the idea prevails that such properties depend on mysterious virtues or vices with which particular clays are primarily endowed. The inference may or may not be true. Similar phenomena occur with other refractories, e.g. magnesite. In any case the tendency to split with abrupt changes of temperature can to a certain extent be controlled by keeping the texture of the firebrick open and coarse-grained.

Silica bricks are particularly liable to this fault whether they be fine or coarse-grained. The phenomenon is here probably connected with thermal conductivity, the coefficient of thermal expansion, and probably also with the specific heat. The continued expansion of the silica grains in silica bricks in furnaces, owing to a slow change in the character of the silica after the brick has been made, accounts for some of the friability of these bricks. In the first fire, the fluxing lime becomes saturated with silica, and the mixture sets; if the set of the grains be afterwards forcibly displaced by internal expansions, the binding agent is materially weakened by the disturbance. A high temperature pre-calcination of all or part of the silica would mitigate the difficulty arising from this particular cause. This is done by some manufacturers, but I do not know if the efficiency of the calcination is checked by specific gravity determinations. Silica bricks made with pre-calcined material do not always "ring" so clearly when struck together.

Fine-grained Firebricks.

Other things being equal, a fine-grained texture gives firebricks the property of resisting abrasion and attack of fluxes, slags, flue dust, salt vapours, etc. Chemical composition here plays an important part, *inter se congruunt similia, configunt dissimilia*—like agrees with like and disagrees with the unlike; otherwise expressed, acidic bricks resist acidic fluxes and basic bricks resist basic fluxes, but basic bricks are rapidly eroded by acidic fluxes and acidic bricks rapidly erode basic bricks. Texture is also of vital importance. The photograph, Fig. 15, and the samples on the table, show very well how corrosive slags attack the bricks with which they are in contact.* The slag was highly basic, the vitreous brick was made from an aluminous clay. The

* B. Moore and J. W. Mellor, *Trans. Eng. Cer. Soc.*, **II**, 178, 1912; *Collected Papers*, **I**, 321, 1914.

conditions in the furnace must have some analogies with two armies face to face. Slight imperfections in the exposed face of the brick are weak spots which are developed by the slag into salients; the salients are widened and deepened; patches are isolated and imprisoned in the slag. In this particular case, the flank attacks by the slag are most serious. The joints separating the bricks from one another are the weakest places. Here the slag may cut its way until the brick itself is undermined and isolated. Ultimately the brick leaves the setting, rises, and floats on the surface of the slag. Naturally, the use of large bricks would lessen the number of joints, but if the slabs be too large they are particularly liable to crack, and a crack may cause more damage than quite a number of joints. This example emphasizes very forcibly the well-known fact that bricks which have to resist the corrosive action of slag should have a close texture and be of uniform size, so that the joints are as small as practicable. The jointing clay should also be chosen so that it quickly vitrifies without cracking and welds the bricks together when the furnace is fired for the first time. If two bricks made with the same material, one made with a close and one with an open texture, be exposed to the vapour of salt for some time, it will appear as if the close-textured brick is most attacked, because it will be covered with a thin film of glaze, while the open-textured brick will not appear to be so much attacked. However, if two sections be examined it will be found that the vapours have penetrated perhaps half an inch into the interior of the open-textured brick and not one-sixteenth of an inch into the close-textured brick. Presumably if the action were continued for a longer time, the whole face of the open-textured brick would collapse, while the glazed face of the close-textured brick would remain intact behind the glazed surface film. [Samples shown.] In the two white samples on the table, both pieces have been exposed to the same corrosive vapours, but the less porous piece is more attacked than the other. This is because the less porous body is far more silicious than the other one, and, other things being equal, siliceous bodies favour rapid attack by salt vapours—aluminous bodies are not so readily attacked. Obviously, therefore, if both these factors—chemical composition and texture—be not simultaneously considered, contradictory or cross results may be obtained. The so-called acid-resisting bricks must also have a close-grained vitreous texture, illustrated by the samples Figs. 8 and 9. Similar remarks apply to the glass-house pot, Fig. 11.

Applications.

We are all aware of the difficulty in laying down general rules with respect to clays, since, taken individually, clays from different deposits have a remarkably varied character. In spite of this, I felt that probably more good would obtain if I opened this discussion by trying to show that the texture of a firebrick is virtually as important as refractoriness and chemical composition. The texture can be largely controlled by the manufacturer. The consumer has to carefully consider the conditions which prevail in different parts of any particular furnace before he selects for trial particular types of firebrick as likely to suit particular parts of his furnace.

Consider the lining of a blast furnace. The bricks near the top of the furnace are not exposed to high temperatures, but there they have to withstand a certain amount of abrasion, impact, and change of temperature. The bricks are liable to spalling and disintegration, due, as is supposed, to the deposition of carbon formed by reactions between the iron oxide in the brick and the furnace gases. Nodules or patches of iron

oxide in the bricks are more liable to serious trouble than is the case when the iron oxide is more uniformly diffused throughout the mass, possibly because, in the latter case, the iron oxides are fixed by the aluminosilicates of the brick, and they then resist better the action of the furnace gases. The bricks should also be close and compact; such bricks are usually tough and are not so permeable to gases. The temperature conditions become increasingly severe in descending the furnace. The upper parts of the lining are normally protected to some extent by the development of a surface film of carbon, but the friction of the descending charge and the impact of fine particles of solid carried forward by the blast may produce erosion, particularly if concentrated in local parts. The bricks in the mid zone are also exposed to the slagging effects of particles of salt and other basic fluxes from the coke, etc. There are no very abrupt temperature changes, so that a close-textured compact brick is desirable for this region. The conditions which prevail in the hearth and bosh require a very special brick to withstand high temperature, to resist the scouring action of highly basic molten slag, and a rather heavy mechanical load; the volume changes should be small, since the bricks must be tight without leakage; but there is comparatively little wear and tear by abrasion. The stove bricks should have a high thermal capacity, so that they can absorb and give up the largest possible amounts of heat and be capable of resisting the sand-blasting action of flue dust. I do not know if the former quality can be controlled by the manufacturer, although the remarkable rise in the specific heat of firebricks with temperature is worthy of note.* It will, however, be clear that the *mechanical resistance* of a firebrick to the cutting action of swift streams of flue dust can be to some extent controlled by the manufacturer. The *chemical resistance* of a firebrick to different types of flue dust is largely determined by the chemical composition of the fire-clay—excluding, of course, the cases where special basic bricks are required. For instance, other things being equal, ferruginous coal ashes in a stream of burning producer gas will have a more severe action on siliceous than on aluminous bricks.†

Other furnaces might also be discussed in a similar manner.‡ The special conditions which prevail in particular furnaces or in particular parts of a furnace must be approximately known before an attempt can be made to indicate the type of firebricks likely to prove most suitable. I have purposely kept away from the effects of reducing gases on firebricks, because that subject is under investigation.

* S. T. Wilson, A. D. Holdcroft, and J. W. Mellor, *Trans. Eng. Cer. Soc.*, **12**, 279, 1913; *Collected Papers*, **1**, 83, 1914.

† *Vide* J. W. Mellor, *Trans. Eng. Cer. Soc.*, **13**, 12, 1913; *Collected Papers*, **1**, 347, 1914.

‡ E. F. Dürre, *Tonind. Ztg.*, **19**, 379, 411, 424, 459, 474, 490, 1895; P. Jochum, *ibid.*, **27**, 335, 1903; M. Störmer, *ibid.*, **31**, 523, 1907; B. Osann, *ibid.*, **27**, 336, 775, 1903; **30**, 145, 1906; **31**, 1382, 1907; *Stahl und Eisen*, **23**, 826, 1903; **26**, 336, 1906; **27**, 1626, 1907; F. W. Lürmann, *ibid.*, **12**, 265, 1892; **18**, 168, 1898; T. Ludwig, *ibid.*, **25**, 870, 1905; H. Kinder, *ibid.*, **32**, 231, 1912; E. Blasberg, *ibid.*, **30**, 1055, 1910; O. Sommersbach, *ibid.*, **33**, 2027, 2077, 2120, 1913; F. Firmstone, *Trans. Amer. Inst. Min. Eng.*, **34**, 427, 1904; T. Holgate, *Journ. Gas Lighting*, **91**, 170, 230, 1905; *Chem. Eng.*, **22**, 148, 1915; W. H. Kelley, *ibid.*, **22**, 82, 1915; G. Rigg, *Met. Chem. Eng.*, **8**, 237, 1910; J. C. Bailar, *ibid.*, **8**, 517, 611, 1910; Anon., *Brick*, **31**, 317, 1909; Anon., *Electrochem. Met. Ind.*, **5**, 152, 1907.

THE APPLICATION OF PETROGRAPHIC METHODS TO THE STUDY OF REFRACTORY MATERIALS.

The **President** asked **Professor Fearnside** to follow Dr. Mellor with his Paper on "The Application of Petrographic Methods to the Study of Refractory Materials."

Professor W. G. Fearnside (University of Sheffield): I regret that my contribution to this discussion is quite unworthy of the name of a paper, and that if as a paper it exists at all it is only in my head. I had expected to speak after Mr. Johns, who is to address you on the subject of the physical behaviour of silica at high temperatures, and I had arranged with him the text of the subject which I proposed to follow. I do, however, welcome the opportunity to say a word or two about certain matters concerning the study of refractory materials, and having heard what previous speakers have said about details, I should like to say something about general policy and the direction in which refractory makers and scientific people together may hope to advance. During the last two or three years, in fact since the beginning of the war, it has been my lot to visit a good many works, both of the consumers of refractory materials and of those who are makers of them, and in going the round of these various places I have arrived at a very definite point of view. I consider that if it were possible for the best practice as carried out in the most up-to-date works of refractory material makers, and the best schemes for the selection of materials as adopted by those who have been most successful in their works, to be correlated, and they alone be permitted to continue in any of the works, the refractory industry in this country would have gone far. In my opinion one of the pressing necessities in this matter is that the users of refractory materials and the makers of them should be brought together, with scientific people to advise them, and that those who make should be given opportunities to see the purpose and mode of application of the particular articles which they manufacture, and that those who complain that the materials delivered to them are not so good as they ought to be, or are quite unsuitable for the purpose for which they use them, should see for themselves what are the difficulties with which the makers have to contend. If the two separated interests could be brought together, and if alongside there were a competent and sympathetic man of science who would stand by and hold the balance and occasionally give his help to spoke a wheel, the progress of the refractory-making industry would be more rapid than many people think.

Among scientific workers, in my opinion there has been in the past most lamentable failure to recognize how much good information is locked up in the experience of the foremen in the works. Foremen do not talk of pyrometers and temperatures, but it may be that by dropping water on a brick they learn to estimate instantaneously the temperature more nearly than people who lack the necessary experience could in a day, even with the best pyrometer obtainable. Works estimation of temperatures is often accomplished by foremen with an exactitude that many so-called scientific laboratories never approach. I think also that there is much good information locked up in the understanding of those who handle materials as they are received into the works. One sees an experienced workman look at a batch of material and say "that is no good." Workmen may make their remarks in other language, but they are generally right, and I have found that if one cross-examines them—and they are generally willing to answer questions—one gains information about the importance of small details which in the

language of a scientific paper it would take a great deal of script to express. I judge that the observations made by the experienced workman are at least as accurate as those made under the best conditions of laboratory experiment. I quite agree that the practice of refractory manufacture has become more of an art than a scientific process, and, as in most things connected with art, some individuals do better work than others. It is the art of the best craftsmen that I wish to see made a subject for scientific observation; and if the reasons which have brought the craftsmen of whom I have been speaking to adopt the arts which they practise could be ascertained by scientific analysis, and the information could be put on paper and circulated as common knowledge, I think we should have a sound basis for research upon refractory materials, from which advance would proceed at a very rapid rate.

I had promised to say a word about the application of the microscope to the study of refractory materials, and in opening this subject I wish to recall the work done on the microscopic study of rocks more than fifty years ago by the late Henry Clifton Sorby, of Sheffield. Sorby not only told us how to begin, he went further than many of us at the present day are able to realize, in the application of the microscope to the study of the constitution and physical structure of rocks and of many other composite materials. The study of composite materials in which the texture is coarse grained is comparatively easy, but Sorby also studied materials in which the grain is fine. Sorby applied his microscope both to materials which he could rub down to a condition of transparency and to opaque materials, such as metals, which would give him polished surfaces. He learned a good deal of the art of preparing his own specimens, and he showed other people how, from a thin slice of a rock, or from a polished specimen of a metal, they might judge the strengths and most of the other physical properties of almost any material which will survive the somewhat drastic process of polishing to a flat surface. Along with rocks and metals, Sorby started to apply his methods to the study of manufactured refractory materials, and in the years prior to 1870 he attempted to prepare some thin sections of silica bricks, which, however, by reason of the friability of the material, were not particularly successful. In my laboratory at Sheffield I have tried to repeat Sorby's experiments upon various manufactured refractory materials, and I have tried to cultivate the technique which is required to reduce slabs cut from refractory bricks, stoppers, and crucibles, as received from manufacturers, to a condition of transparency. I find, however, that this technique is not easy. My own fingers are not sufficiently sensitive to hold the sections of bricks which have been rubbed down to the thinness which I required. From ordinary tough rocks we obtain slices of rock about one-thousandth of an inch in thickness, but even these we break not infrequently in finishing, even when we have spent several hours' work upon them, and one of the most pressing necessities in this country at the moment, both for the study of refractory and other sorts of rock materials with the microscope, is that some business firm should learn the required technique and take up for profit the preparation of really thin transparent slices of mineral materials on a commercial scale. I regret to say that such preparation of specimens is one of the "key industries" for which prior to the war we have depended upon another country. It seems as if every one here is afraid of the difficulties of the technique and of the monotony of the process, and, from the national point of view, it is high time somebody took it up. The difficulties are not of an insuperable kind, and in rubbed-down specimens of refractory bricks made from basic materials, in which high refractive index is a characteristic property of the

mineral constituents—I allude to magnesite, chromite, bauxite, zirconia, and the like—one can see enough in slices which one has made oneself to judge at a glance the measure of success which the maker of the brick has attained, and with experience to guide one it is not difficult to foretell approximately how particular batches of bricks will behave when they come to be built into the walls or roof of a furnace.

The President has said a few words on the necessity for uniformity of quality of refractory materials being controlled by specification of chemical analysis. In basic bricks the chemical analysis tells us a good deal, but bulk composition is not by any means the most essential factor in determining the behaviour of every kind of brick when they are in use in the furnace. The material of which most bricks are manufactured may be regarded as consisting of two grades or texture, the one, which we may speak of as the plums, enclosed in the other, which we may allude to as porridge. The refractory properties of most of the coarse-textured materials which are used to form the plums is fairly well understood, but in the porridge, or material which is between the plums, there are mixtures of many chemically different materials, and in firing, chemical reactions are prone to occur which make the refractory properties of the fired product totally different from those of any of its constituents. The great use of the microscope is to note what has happened at boundaries where, in the porridge, distinct chemical entities meet, and when bricks made from such materials as magnesite, chromite, and zirconia, which have failed in service, are rubbed down to transparency and examined with the aid of the petrographic microscope, the cause of the failure, which lies in the weakness of the junctions between the main constituent and the material used to bind it, is easy to observe. In dealing with acid materials, the technique of thin slice making is more difficult than with the basic. The materials are more tender. Minerals containing a high percentage of silica have comparatively low refractive indices, and without a great deal of experience it is difficult to be certain of even such important differences as those between quartz and feldspar, or between quartz and the polymorphic forms of silica, tridymite and cristobalite. There are, however, other methods of dealing with these low refractive index materials, which with certainty give results to four places of decimals. By observations upon the crushed material with the refractometer one easily learns to distinguish between the quartz and tridymite contained in silica bricks as manufactured, and by a mere inspection of the powder immersed in various liquids under the microscope one gains a very excellent and very correct idea of the amount of heat treatment that the brick has received. With new-made firebricks one does not yet succeed so easily, for in firebricks newly made, or which have not been fired more than a few scores or hundreds of hours, the texture is so fine grained that in slices the thickness of which is about $1/500$ th or even only $1/1,000$ th of an inch, the mineral constituents are in such tiny crystals that they appear as felted fibres which generally interfere one with another and appear as a fabric in which, though one expects with higher powers always to see more, one always fails to see as much as one would wish. With the possibility that experts sometime will succeed in cutting the slices thinner, I have no doubt at all that eventually we shall find means to determine with the microscope the structure of firebricks and of porcelain. More satisfactory specimens, from the point of view of demonstration, are micro-preparations cut from the bricks discarded when the linings of larger furnaces are dismantled at the termination of their run, and probably it is by careful selection and the scientific study of these highly metamorphosed end-products which have been suc-

cessful, that scientific workers will be able to gain information which may suggest a probable direction for the refractory manufacturers' next advance. From furnaces which are falling to pieces after a long and very successful life, recrystallized rock-forming materials, which under the microscope are the most beautiful of objects, may frequently be obtained. In such materials occur well formed crystals, the composition of which is determinate without chemical analysis, and in five or six minutes results which in the ordinary way the chemist would only get in three or four hours' continuous work are obtainable by inspection by the expert with the microscope. The study of refractory materials by the microscope is a method which promises to go far, and I think that when its application is generally adopted by makers and users of refractory materials it will not be very long before, to further their own interests, the makers of refractory plum-porridges learn to see to it that the porridge which they use is suitable for holding the plums together. Already we know a great deal about the plums, but I fear we are still exceedingly ignorant as to the constitution of the porridges. There are materials which when put into bricks remain, but there are materials which form inside the bricks when and after the bricks are being made and by chemical re-adjustments after the brick has been put into use. Just as at ordinary temperatures it is impossible to keep hydrochloric acid and ammonia in one and the same bottle at the same time, so in bricks at high temperatures many materials re-act and undergo chemical change, and what we put into the brick is not what remains in the brick when it has been fired and is in service. I commend the microscopic method of attack because I think it has great possibilities, and I am sure that as a method of obtaining real information about the composition and texture of manufactured refractory materials it ought to be adopted extensively.

Dr. Cecil H. Desch (Glasgow) wrote that Professor Fearnside, in his account of the method of microscopical examination in the study of refractories, had not made any reference to the examination of polished and etched surfaces by reflected light. The writer had found the greatest difficulty in grinding sections of slags, cement clinker, and similar substances sufficiently thin to bear examination by the usual optical methods in transmitted light. It was not merely a matter of want of skill, as he had sent some of the specimens to leading petrological firms here and abroad, and had found even their thinnest sections too thick to bear examination under the required magnification. He had therefore adopted the method of grinding one surface only of the specimen in the usual manner for petrological work, and examining in the etched or unetched condition by means of a metallographic microscope with a vertical illuminator. The low reflecting power of fire-brick, slag, and other similar materials presented a certain difficulty, as the surface was apt to be obscured by diffused light, which interfered with the examination of detail, but this could be overcome by regulating the lenses and diaphragms on the optical bench. He had in this way obtained sharp photographs of a eutectic structure in Portland cement clinker which was quite invisible in thin sections of the same clinker, owing to the elements of the structure being of less size than the thickness of the section. He had examined the stony, opaque varieties of slag in the same manner, with entire success, and felt sure that the method might equally well be applied to refractories. The different constituents could be distinguished by etching with dilute hydrofluoric acid or other reagent. Dr. Mellor's Paper has shown that excellent photographs of polished surfaces could be obtained for macroscopical examination, and the same method would be found of great value for the microscopical study

THE EXAMINATION OF THE TEXTURE OF UNFIRED REFRACTORIES.

At this point the **President** asked **Dr. R. Lessing** to show a series of specimens illustrating a method of testing he had devised five or six years ago for ascertaining the texture and rational composition of refractory mixtures before firing.

Dr. R. Lessing : The examination of the texture of finished refractories does not lend itself to quantitative treatment. Whilst a good deal of information on the rational composition and the mode of bondage can be gained by cutting and grinding sections of the fired goods, the quantitative ratio of such main constituents as "grog" and binding clay can only be estimated very roughly. In cases where the "grog" originally consisted of the same material as the binder, the difficulty of discriminating between the two in the fired state is still further accentuated and may make even such approximation impossible.

The importance of the relation of "grog," i.e. the previously fired constituent which forms the skeleton and the "green" clay which provides the binding matrix for the "grog," warranted the elaboration of a method for the quantitative separation of the goods before they undergo the final firing, or of the mixtures employed for moulding the articles.

The method devised consists of a simple process of elutriation by which the true clay substance of the "green" clay is removed by a gentle current of water and separated from the water by allowing it to settle out on standing. The rate of flow of water is so adjusted that the "grog" and also the heavy and coarse-grained residue of the "green" clay, consisting of sand, shale, or carbonaceous substances, are left behind in the elutriating vessel.

Elutriation is continued until the last clouds of clay substance are removed and the water becomes perfectly clear with the lightest portions of the residue floating just below the outlet.

A very simple form of elutriator accurate enough for works purposes consists of a tall glass cylinder, into which the water is passed through a glass tube reaching nearly to the bottom. The cylinder is placed in a bucket into which the clay suspension overflows, and from which the clear water is syphoned off after settling. For the purpose of the test, about 500 grams of the sample (which may be taken before or after "tempering," or from a moulded body before or after drying) are well soaked in water and washed into the cylinder. The resultant products of clay and residue are dried, and a screening test is then performed on the residue, from which the texture of the body and the ratio of "grog," granular (uncrushed) clay, shale, and coal can be ascertained.

The fractions from the screening test and the dried clay slip are weighed, and their percentage of the total is ascertained. A small portion of the sample is submitted to a moisture test, and all the figures obtained are reduced to the "dry" basis.

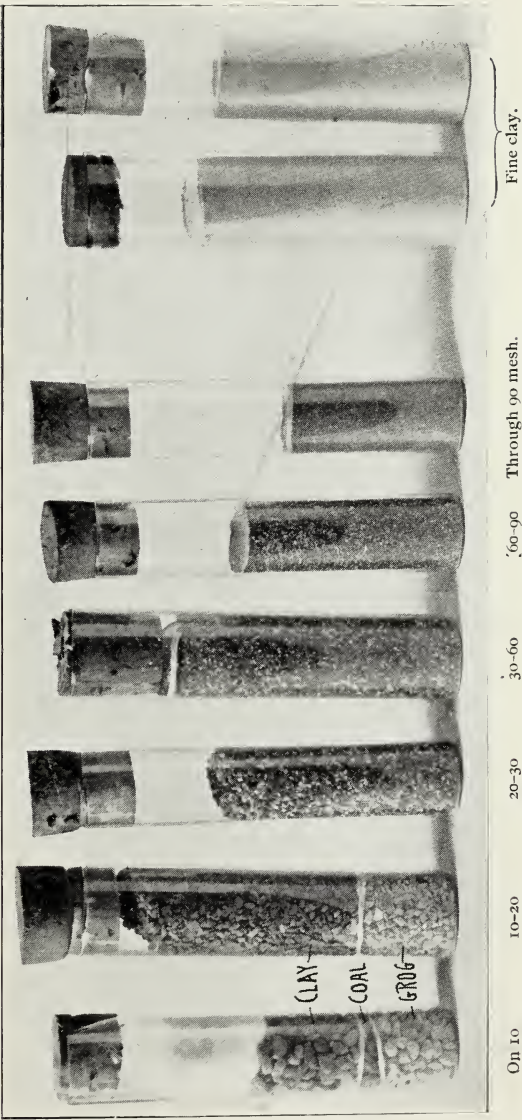


FIG. 1.—Retort Mixture from Stourbridge District before adoption of Standard Specification.

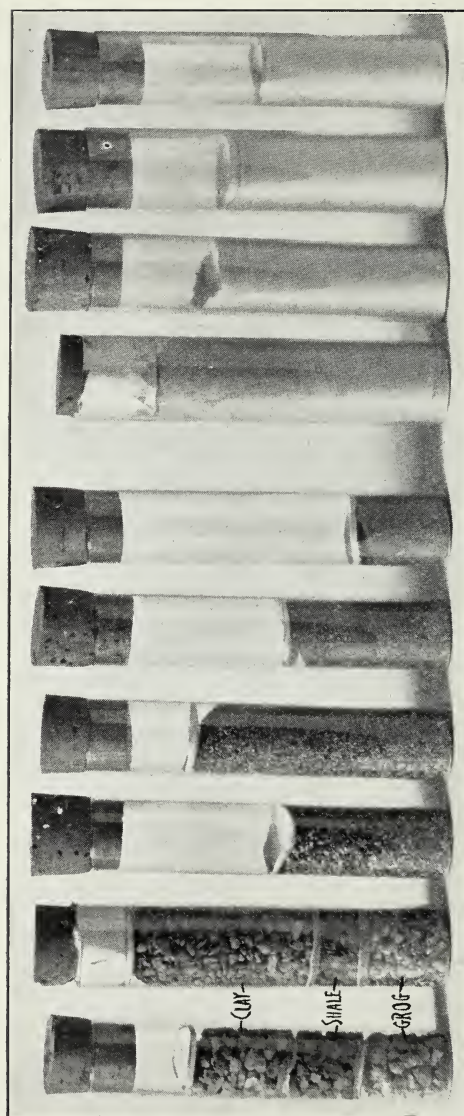


FIG. 2.—Retort Mixture from Glenboig District before adoption of Standard Specification.

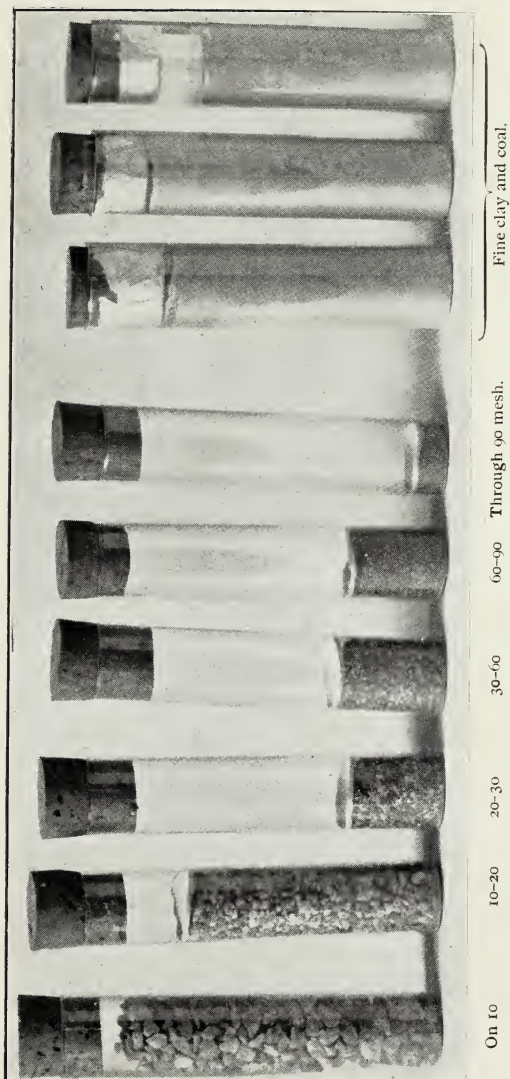


FIG. 3.—Retort Mixture from Stourbridge District after adoption of Standard Specification.

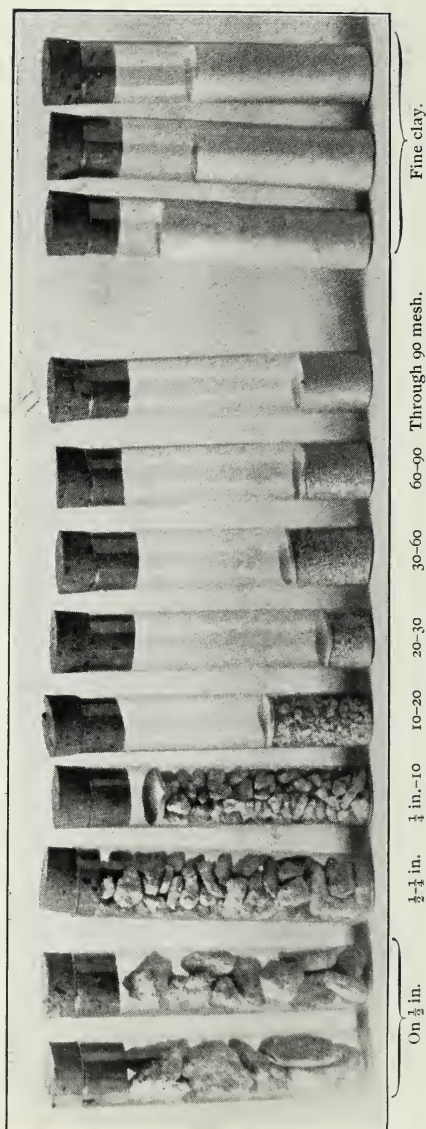


FIG. 4.—German Retort Mixture.

The fractions not passing through a twenty-mesh sieve contain particles which can be separated by hand-picking into such constituents as "grog," uncrushed "green" clay, shale, or coal. The "grog" itself may be further separated into broken brick, saggar, virgin clay, or other natural rock. Each sub-fraction is weighed and its percentage of the main fraction and of the total is ascertained. Where required, each constituent can be submitted to chemical analysis or physical tests.

The rational composition of the fractions can usually be ascertained with sufficient accuracy by estimating the proportion of light-coloured to dark-coloured particles by their appearance.

In cases where the type of raw materials used is known, such as in ordinary works control, a set of standard mixtures of varying proportions of "grog" and clay residue of each size can be prepared and forms a useful guide for comparison.

The results obtained from four typical samples are recorded below. In order to show the type of products obtained in the test, the photographs of the corresponding specimens are reproduced in Figs. 1-4. The samples represent :—

1. Gas retort mixture from Stourbridge district before adoption of Gas Engineers' standard specification.
2. Gas retort mixture from Glenboig district before adoption of standard specification.
3. Gas retort mixture from Stourbridge district after adoption of standard specification.
4. Gas retort mixture from German firebrick works.

			1.	2.	3.	4.	
Plus $\frac{1}{2}$ in.	—	—	—	21.4	per cent.
$\frac{1}{2}$ in.— $\frac{1}{4}$ in.	—	—	—	17.0	"
$\frac{1}{4}$ in.—10 mesh	8.8	9.0	15.6	10.0	"
10—20 mesh	19.9	17.5	10.6	4.4	"
20—30 mesh	10.6	7.0	3.6	1.9	"
30—60 mesh	15.8	11.0	4.4	3.8	"
60—90 mesh	8.8	7.0	3.4	3.7	"
Minus 90 mesh	7.7	4.0	1.7	3.8	"
Fine clay	28.4	44.5	60.7	34.0	"
			100.0	100.0	100.0	100.0	"
Grog, plus 20 mesh	8.5	6.8	25.7	52.8	"
Grog, minus 20 mesh	13.4	9.9	7.3	10.2	"
Coarse clay and residue	49.7	38.8	6.3	3.0	"
Fine clay	28.4	44.5	60.7	34.0	"
			100.0	100.0	100.0	100.0	"

From a combined examination of the figures and the photographs of the actual fractions obtained great differences will be observed in the composition of the various mixtures.

Samples 1 and 2 are typical of the manufacture of fireclay goods as carried on in this country before the adoption of the standard specification issued by the joint committee of the Institution of Gas Engineers and the Society of British Gas Industries. The outstanding feature in both samples from the two principal manufacturing districts is the small percentage of useful

"grog." The preparation of the mixtures according to the old manufacturing method consisted in crushing and grinding the "green" clay together with "grog," which usually consisted of "wasters" in roller mills. In consequence a large proportion of the "grog" added was crushed to small size and dust, in which form it did not fulfil its proper function of supplying a rigid skeleton to the final product. On the other hand, a good deal of the "green" clay, being of a somewhat more elastic nature, escaped the grinding action, and was left in the form of granules of considerable size. These granules instead of acting as binder and embedding agent for the grog, formed themselves a skeleton which, however, was not rigid, but was subject to considerable shrinkage both in the drying stove and the fire kiln.

In order to comply with the requirements of the standard specification it is necessary to grind "grog" and "green" clay separately. This permits of the required grading of the "grog," the removal of fine dust from it, and the reduction of the "green" clay to fine powder. As will be seen from Fig. 3, the granular clay or shale and carbonaceous matter have disappeared entirely from the largest sizes of the mixture. The total percentage of "grog" has increased, and the proportion of fine to coarse "grog" has considerably decreased.

For comparison the results of a test carried out on a German gas retort mixture are recorded. They show that it is possible with a proper preliminary treatment of the ingredients to add a very much larger proportion of "grog" than has ever been attempted by the British makers, and at the same time considerably increase the size of the particles. The ratio of "grog" to "green" clay, which is about 1 : 2 in sample 3, is practically reversed to 2 : 1 in the German mixture.

Considering that the comparatively small increase from about 20 per cent. to 35 per cent. led in some cases at the start to the output of goods of doubtful mechanical strength, the conditions for the successful working up of a mixture, such as shown in No. 4 test, should be inquired into. It is evident from the results of the test that the binding clay had probably been submitted to washing in order to increase its plasticity—hence the small percentage of clay residue. Further, it could be seen from the sample itself, and from the close adherence of the binding clay to the "grog" during elutriation, that the mixture had undergone a rather more thorough mechanical treatment and maturing process than was usual in English procedure up to quite recently.

From the examples quoted it will be seen that the test proposed, which has now been in use for about six years, can be profitably applied to the examination of unfired refractories of unknown composition. The principal use of the method is, however, for works purposes, and it affords a very simple means for the daily control of manufacturing operations from the mixing-pan to the kiln.

THE WORK OF THE JOINT REFRACTORY MATERIALS COMMITTEE.

The President : I will now call upon **Dr. H. G. Colman** to speak on the work of the Joint Refractory Materials Committee of the Institution of Gas Engineers and the Society of British Gas Industries. We are very much indebted to him for the excellent work that he has done in connection with this Joint Refractory Committee, and we are very fortunate in having him present with us this evening.

Dr. H. G. Colman : I have been asked to contribute to the discussion an account of the work of the Joint Refractory Materials Committee of the Institution of Gas Engineers and the Society of British Gas Industries during the past few years, and in compliance with that request I will give a general outline of the work they have carried out. Owing to the increase in working temperatures employed in gasworks retort settings for many years past, increasing difficulties have been experienced in obtaining fire-resisting materials of fully reliable quality for such temperatures, and following the reading and discussion of the valuable paper on "Refractory Materials" by F. J. Bywater at the Annual Meeting of the Institution of Gas Engineers in 1908, a Joint Committee was formed consisting of members nominated by the former Institution on behalf of the users, and by the Society of British Gas Industries on behalf of the manufacturers of such materials. Mr. Bywater was appointed Honorary Secretary, and Dr. J. W. Mellor accepted the position of Technical Adviser, and on these two has fallen the lion's share of the work. The main work of the Committee has been (1) the drawing up of a standard specification for the various classes of materials commonly employed in gasworks, and the prescription of the various tests with which such goods should comply for these purposes, and (2) the carrying out, as far as means allowed, of research work on matters likely to yield information of value both to manufacturers and users, and to help towards the main end for which the Committee was formed, namely, the provision of refractory goods of the most suitable qualities for the particular purpose required. The matter of the standard specification was dealt with first, and to assist in drawing it up a number of typical gasworks were selected. Investigations were made at these works to determine as exactly as practicable the maximum temperatures attained in the various parts of the furnace plant and the extent and rate of the temperature fluctuations which occur. Simultaneously, tests for refractoriness, permanent expansion and contraction, porosity, etc., were carried out on a large number of samples of the material at that time obtainable from the different manufacturers. In laying down the conditions of the specification, the Committee recognized from the outset that it was impossible to lay down tests of such stringency as would be required for an ideal material, but that at the commencement the tests laid down must be such as could be complied with under the existing conditions of manufacture. The tests prescribed were, therefore, such as it had been found from the above investigation would be complied with by the better-class material then available, but which would rule

out the less satisfactory material. The intention is to revise the specification periodically in the direction of greater stringency as the technique of the firebrick manufacture advances, and to modify the prescriptions given for making the various tests for the material as increased knowledge on this point allows this to be done with advantage. Except in one small point, which I will refer to later, no stipulations were made in the specification as to the methods of manufacture, this being left to manufacturers themselves, subject, of course, to the products made complying with the prescribed tests. In the specification (see Appendix I, p. 180) three different classes of material are dealt with, namely, retort material, ordinary firebricks or blocks, the silica content of which is less than 80 per cent. and in most cases less than 75 per cent., and silica-bricks, these being divided further into the true silica bricks containing 92 per cent. or more of silica, and those containing only 80-92 per cent. of silica, termed for distinction "siliceous bricks." Retort material presented exceptional difficulties, owing to the great and rapid temperature fluctuations to which it was subjected, due to the retorts being filled at frequent intervals with a large mass of cold coal when at a temperature of 1,000°C. or higher. To withstand this rapid change of temperature an open porous structure was required in addition to refractoriness and freedom from excessive permanent contraction or expansion, etc., and in this case a minimum degree of porosity was also specified. With this material also occurred the only case in which methods of manufacture were mentioned, the prescription being made that the fine dust should be removed from the grog used in the manufacture of the retorts. With retort material, difficulties in respect of lack of refractoriness have not been very frequent, but much greater difficulties arose from lack of mechanical strength of the retorts, resulting in fractures of the retorts in transit and in course of erection, and subsequent development of cracks under the strains set up in the hot furnaces and the rapid alterations of temperature due to their periodic charging with cold coal, and there is much room for improvement in manufacture to obviate these defects. In the case of ordinary firebrick material, specifications were given for two grades of material for use in different portions of the retort settings, according to the maximum temperature they were required to withstand. Since the publication of the specification, tests made on the materials supplied by manufacturers have shown that in the greater part of the material available a steady improvement has taken place in the refractoriness and the amount of permanent expansion or contraction shown on tests by the goods, and the specified tests in these respects could be considerably stiffened without materially reducing the amount of material which would be available. The question of the extent to which any such stiffening up of the tests should be made was bound up with the further question of the exact conditions under which such tests are to be made, the investigation of which point was not complete, and on that account no alteration in the allowable limits has yet been made. With respect to "siliceous bricks," i.e. bricks containing 80 to 90 per cent. of silica, matters have moved rapidly since the specification was drawn up: very considerable developments in this class of brick have taken place both in this country and in the United States, and the whole of this section required consideration. The second object of the Committee, namely, the carrying on of research work on the subject, has been proceeded with throughout the last few years, so far as the means at the disposal of the Committee have allowed. The limited funds available, and the fact that they have themselves no properly equipped laboratory at their command, have, however, precluded their undertaking such work to the extent they would have desired, and that they

have been able to proceed in that direction as far as they have been largely due to the co-operation and help of the Stoke-on-Trent Education Committee and of Dr. Mellor at the County Pottery Laboratory at Stoke. Their funds have now been increased owing to a grant from the Privy Council Committee on Scientific and Industrial Research. Even with this contribution, however, the available funds only amount to £230 per annum at present, a sum which is quite insufficient to carry out research work to the extent that is required, even so far as the special uses of refractory materials for gasworks and coke ovens are concerned, and quite apart from the wider considerations of the metallurgical and other industries concerned in the matter. For the full investigation the subject urgently required, a much larger sum is required, together with the co-operation of all classes of manufacturers and users of refractory goods. So far as I am able to speak for the Committee I represent, I think I might promise their hearty co-operation with efforts of others in the same direction. The chief matter on which research work has been in progress recently has been that of the influence of pressure on the refractoriness of a firebrick, this being a matter of great importance both from the manufacturing point of view and on the question of the prescribed tests. Generally the material in a setting was under considerable pressure and in contact with a reducing atmosphere. The tests prescribed in the specification, however, were carried out under no pressure and in an oxidizing atmosphere, and as pressure and reducing atmospheres both tend to lower the refractoriness, the tests specified were not carried out under conditions corresponding to those existing in actual work, but under too favourable conditions. When the specification was drawn up, however, whilst this was recognized, no method of test had then been devised for carrying out the tests under load or in the reducing atmosphere which would give reliable and agreeing results, and until such time as suitable tests under these conditions could be devised, the method of testing without load and in an oxidizing atmosphere was specified, and to compensate approximately for these conditions being more favourable than those existing in practice, a minimum degree of refractoriness was specified considerably higher than would have been fixed had it been possible to prescribe a suitable test more nearly representative of the working conditions. The investigation of the effect of load on refractoriness has since been commenced by Dr. Mellor, using in the first place fire-clays of various origin, and the results of the work have been published by Dr. Mellor and Lieutenant Moore in the *Transactions of the English Ceramic Society*, in which they showed that from the results obtained in the investigation of these clays the adverse effect of pressure in refractoriness and the extent of this may be represented fairly closely by an empirical formula. The investigation is now in progress with a much larger apparatus, capable of testing a full-sized brick, and special bricks are being manufactured from different clays with different percentages of grog and fired at known temperatures, as it has been found absolutely necessary that the "life-history" of the brick must be known, which is not possible with bricks obtained in the open market. This necessity, however, involves increased cost and time in carrying out the research. Other investigations are in progress or under consideration on the following points:—

(1) Determination of the differences in size of bricks when cold and when at high temperatures, i.e. the combined effect of the thermal expansion and the "permanent" expansion and contraction.

(2) The cement material employed in retort settings and the influence of the addition thereto of varying proportions of fine grog.

(3) The relative effect of an oxidizing atmosphere and a reducing atmo-

sphere on the refractoriness and permanent expansion or contraction of refractory goods.

(4) The influence of fine flue dust carried into settings on the refractoriness and life of the materials employed.

(5) The effect of admixture of highly siliceous rock (such as ganister) on the working qualities of fire-clay goods.

(6) The effect of firing temperature on the subsequent refractory qualities of the goods.

The necessary apparatus for the investigation of several of these matters has been designed by Dr. Mellor, ordered and in part delivered to the County Pottery Laboratory at Stoke, but the rate of progress which will be made depends largely upon the numbers of workers who can be engaged upon the work.

THE WORK OF THE GEOLOGICAL SURVEY ON REFRACTORY MATERIALS.

The **President** : Before we join in the general Discussion on these Papers, I think there are two gentlemen here whom we should like to hear on a phase of this question which has not been touched upon yet. I refer to **Mr. J. Allen Howe**, who will give us a Paper on "The Recent Work of the Geological Survey on Refractory Materials," and afterwards we will have a few remarks from **Dr. A. Strahan**, the well-known Director of the Geological Survey.

Mr. J. Allen Howe : When war broke out there arose a demand for information as to the supply of various minerals in Great Britain. This demand came from merchants, manufacturers, and Government Departments. In an endeavour to meet it the Director of the Geological Survey at once took steps to organize what was left of his staff so that it might concentrate all its energies upon the investigation first of one mineral group and then of another.

Following this line of action, Dr. Strahan has already produced five Special Reports on the mineral resources of Great Britain, and the next of the series will deal with refractory materials.

This subject is not entirely new to the Geological Survey and Museum ; a good deal of information as to the raw materials is scattered through the Memoirs, but much of it is old and it is difficult to find. Further, I may remind you that the only long series of clay test-pieces ever made in this country—that prepared by the late Mr. George Maw, of Benthall—has been in the Museum for many years, and has often proved of value to inquirers. If there had been some organization of manufacturers and trained experimentalists to take up Maw's work where he left off and follow it up, we should not have felt the need of a meeting like this to-day.

I will now explain very briefly what the Geological Survey has done in preparation for the report on British refractory materials.

It was necessary first to get together samples of the raw materials and at the same time to secure exact information as to the locality whence they were obtained, the geological characters and extent of the deposits, and the special local circumstances attending the extraction. For this purpose the country was blocked out into field-areas, and field-staff units were dispatched to work them out one by one. Since this part of the work was begun, in the summer, a continuous stream of samples has been entering Jermyn Street. These samples have been registered as they came in, a portion of each has been prepared as a permanent Museum record, and the remainder has been set aside for examination.

In carrying out the field work, the plan adopted has been to tackle one by one the principal areas of refractory material production, to visit each of the quarries or mines, and consult the producers of the raw stuff and makers of refractory ware.

One field party started operations in the Sheffield district and worked northward to Durham and Northumberland, while another began in the Stourbridge district, passing thence through the Midlands towards North Wales, Lancashire, and Cumberland. Another party dealt with Scotland, and South Wales is just being finished. Several isolated areas have had to be dealt with separately.

In co-ordination with the visits to producers of refractory materials it was considered expedient to visit in each of the main centres a few of the principal users of the material. The first consultation of this kind took place at the works of Sir Robert Hadfield, by his kind invitation. Since then a number of the great steelworks have been visited, also iron-, copper-, and spelter-works, etc. No special attention was paid to coke ovens or gasworks, because this branch of investigation is in the able hands of the Joint Refractory Materials Committee of the Institution of Gas Engineers and the Society of British Gas Industries, and we particularly desired to avoid overlapping. To the members of this Committee I should like to convey our thanks for their sympathy and help. As was anticipated, these visits to the users have been most helpful, not only in enabling the local field operations to be expedited, but in providing ideas for the prosecution of our investigations. Everywhere, to both producers and users, we have to acknowledge a most cordial reception and ungrudging assistance; the need for this work has been constantly emphasized.

The *material collected* falls naturally into several groups. For example, the ganisters, quartzites, and silica rocks employed in the manufacture of silica bricks form one group, the fire-clays form another, refractory sands and dolomite form two more. A few examples, picked out almost at random, have been placed on the table; they serve to illustrate the variety of the material. The number of samples so far received, exclusive of a selection of typical bricks, is well over fifteen hundred.

With regard to the scope of the Survey's work and the character of the programme the Director has set out to complete, it will be observed that the first stage, that of collecting the raw material and information, is almost completed. The next stage, and this is already well advanced, comprises the putting into shape of the field-notes, the chemical analysis of selected samples, and their petrological, mineralogical, and textural examination. Now this involves a great deal of labour and takes a great deal of time. It may prove to be convenient, therefore, to bring out as rapidly as possible a first portion dealing with ganisters, silica rocks, and the like, to be followed at the earliest moment by a second portion dealing with fire-clays, and so on.

While the Geological Survey is the only permanent organized staff for obtaining geological data from the field, and includes in its daily routine the mineralogical and petrological examination of samples, this class of information would by itself only partially meet the needs of the case. Information is required by the producers and users as to the heat-refractoriness and certain other properties of the raw materials; therefore arrangements are being made by which tests of the temperatures of softening and other important physical characteristics shall be completed for incorporation in the report along with the other data. In short, the Director's object is to produce in one or two handy volumes an account of the raw refractory materials of Great Britain, with information as to their geological position and available resources, their petrological and mineralogical characters, together with strictly comparable data on their chemical and physical properties.

These reports, to be brought out in a limited time by a much reduced staff, will not be the perfect things we desire; gaps will be discovered here and

there, experimental data will not be so full as some may consider necessary, but we hope and believe they will form a really useful basis for future work on British refractory materials.

For the first time in this country there will be a publication dealing *at first hand* with all its refractory materials; for the first time a long series of chemical and physical results will be published which will enable direct comparisons to be made of material from different geological sources. And after the reports are finished it is the Director's desire that it may be possible for the Survey and Museum to continue the record, to fill up gaps, to examine new discoveries on the same lines, and to preserve samples permanently for inspection. It is only by using such an organization that this continuity is attainable.

In such a scheme reference to the methods to be adopted in preparing, blending, or firing the raw materials for specific objects of manufacture will find no place. Nor will there be room for the prosecution of those more academic investigations into the properties of the several forms of silica, the peculiarities of certain clays and sands, or the behaviour of the rarer refractory substances, which are so much to be desired. This large and important field of research lies outside the scope of the inquiry being made by the Geological Survey, and none should know better than the members of this gathering how this branch of the work should be organized and placed upon its feet.

Dr. A. Strahan (Director of the Geological Survey and Museum): It is unnecessary for me to add more than a few remarks to supplement what Mr. Howe has said. The initiation of the Special Reports on the mineral resources of Great Britain upon which the Geological Survey is engaged was the direct outcome of the war. Previously, dependence had been placed upon imports for the supply of several materials of which we had ample resources at our doors. When importation was curtailed it became desirable to make more systematic investigation of those resources than had been done, and to inquire what improvements in the exploitation and preparation of our own raw materials were possible. One result of the inquiry has been to show that our home resources of several minerals are practically inexhaustible. Great Britain probably contains a wider and more varied assemblage of minerals than any other area of equal size in the world, and if, as a result of the cutting off of some of our imports, we are compelled to pay more attention to the products of our own country and to devote greater care to their utilization, the calamity of war will not have been unmitigated. It has been pointed out by Mr. Howe that the Geological Survey is the only permanent organized staff in Britain for the investigation of rocks and minerals in the field. The basis of the work of the Survey lies in the construction of a primary 6-in. geological map of the whole country. In the construction of such a map it becomes necessary to note the characters of all mineral deposits, to distinguish strata and trace their outcrops, even though so doing may appear at the moment unlikely to be of practical use. The advantages of this detailed mapping have, nevertheless, received ample illustration. In the coal measures and millstone grit of Yorkshire and some adjacent counties the outcrops of certain recognizable beds of sandstone were laid down upon the 6-in. maps, in some cases many years ago, and

I am assured that these maps have proved of great service in the exploitation of refractory materials. The same remark applies to the detailed mapping of the millstone grit of South Wales, in which occurs the well-known silica rock, and to other materials generally which occur as members of our series of stratified rocks in various parts of the country, such, for example, as iron ores, salt, gypsum, etc. The work of the Survey in the investigation of refractory products consists essentially in determining the reserves and characters of the raw materials. The reserves are large and include nearly all, if not all, the varieties required for industrial purposes, for among them appear the numerous classes of ganister of the coal measures, the silica rocks of our millstone grit and other formations, the quartzites which are developed in some of the older geological systems, fire-clays, sands from many sources, and the dolomitic limestones of which we possess an abundance. British sands and their uses in various industries have been made the subject of study for some years past by Dr. Boswell, of the Imperial College of Science and Technology, and I understand that we may look forward to the publication in the near future of the valuable observations made by him. The object of the work upon which the Geological Survey is now engaged will be to put the manufacturer in possession of a knowledge of the localities where the reserves of refractory materials occur, and of the chemical composition and physical characters of each of the rocks. The rocks themselves will be illustrated in the Museum by a selected set of characteristic specimens taking its place among sets illustrative of our other mineral products. It will remain for the manufacturer to ascertain which of the occurrences can be worked profitably, and which of the materials, or what combination of them, will best suit his purpose. The demand for the earlier volumes of our Special Reports has been keen, and the cordial reception accorded to members of our staff in works throughout the country during the present investigations encourages me to believe that the volume on refractories will be of use in the development of an industry which is important at all times, and at the present time a matter of urgency. This conference will be of the greatest service in helping us to realize the requirements of manufacturers and the directions in which further research should be made.

The President : We have now heard about the resources of our own little country, but we must not overlook the much larger area outside, namely, the Empire. We have here **Mr. T. Crook**, of the Imperial Institute, and perhaps he will say a few words.

Mr. T. Crook referred to the work of the Imperial Institute in connection with an exhibit of refractory materials. The Imperial Institute had been for many years engaged in investigations connected with the mineral resources of the Empire, partly by means of mineral surveys and partly by means of the laboratory investigation of minerals.

The specimens from the Imperial Institute collections exhibited at the meeting had been selected to illustrate the resources of the Empire with regard to the less common refractory materials, including graphite, chromite, bauxite, magnesite, talc, pyrophyllite, and zircon. It is worthy of note that as regards its resources in these less common refractory materials, the Empire is in quite a strong position.

Ceylon is well known as a source of supply of valuable graphite. The Ceylon graphite is of exceptionally good quality, both as regards composition and texture, its flaky or fibrous character giving it special value to crucible-makers. Canada has considerable reserves. Graphite is also abundant in various parts of Africa. The flaky variety is found in some abundance in a disseminated condition among the old rocks of East Africa, Nyasaland, and other parts, and a lower-grade amorphous variety, for which it might be possible to find some use, occurs in Natal. In the United States they use low-grade graphite for foundry purposes, but in this country they had been unable to get people to take it up.

Of chromite, which is chiefly valuable as an ore of chromium, the Empire has ample resources. Rhodesia produces a large share of the world's output, and India contributes a substantial amount from deposits in Baluchistan and Mysore. Quebec, Newfoundland, and other parts of the Empire have considerable reserves.

Bauxite is another refractory with which the Empire is very well provided. The Antrim deposits are well known; but the large reserves of the Jubbulpore and Balaghat districts of the Central Provinces and other parts of India, from which very little has hitherto been produced, are less well known. Of the other deposits within the Empire, perhaps the most interesting at the present time are those of British Guiana, where bauxite of good quality, containing up to 66 per cent. of alumina, is stated to occur in large deposits on the Demerara River, as at Christianburg. North American capitalists have recently given close attention to these deposits, which may be expected to figure in the bauxite production of the near future.

Magnesite, for supplies of which the world has been largely dependent on Austria and Greece, is well represented in the Empire's mineral resources. India has produced considerable amounts for some years past from the Chalk Hills deposits in the Salem district in Southern India, and deposits are now being worked in Mysore. There are deposits of importance at Malelane in the Transvaal, at Heathcote in Victoria (Australia), Fifield in New South Wales, and various parts of Canada, notably Quebec and British Columbia. The deposit at Atlin in British Columbia is hydromagnesite, and contains about 20 per cent. of water, but there is a large amount of it, and as it contains very little lime or other impurities it should yield a good product when calcined. A deposit of magnesite has been worked recently near Tumby Bay, in South Australia.

Talc and pyrophyllite are of some interest as refractories, though less important than the minerals already mentioned. There are large supplies of talc of good quality in Central India, the Transvaal, and elsewhere. Newfoundland and Vancouver Island have deposits of pyrophyllite. It is of interest to note that a quartzose pyrophyllite in Vancouver Island has been quarried for some years for use as a refractory material. It is mixed with clays and shales to produce a fire-clay.

Zirconia, which is now in much request as a high-grade refractory, is obtained in the form of impure baddeleyite from deposits in Minas Geraes, Brazil. The mineral occurs in Ceylon, but hitherto has been found only in small quantities, though it is possible that it may be found in Ceylon mixed with the commoner mineral zircon in sufficient amount to make it of some interest.

Zirconia was formerly obtained from the mineral zircon, which contains up to 67 per cent. of zirconia. In connection with the possibility of producing a zirconia refractory from zircon, it is noteworthy that large supplies of zircon could probably be obtained from sources within the

Empire. Large quantities of the mineral occur in the pegmatite veins and gem gravels of Ceylon, specimens of which were exhibited. Specimens were also exhibited from Zululand, New South Wales, and the Federated Malay States, from which sources it may be possible to obtain supplies.

Monazite sands provide a possible source of cheap zircon. The non-magnetic residue obtained in working monazite concentrates, such as those of the Travancore coast in India, consists largely of fine-grained zircon, and this might be available at very cheap rates as a by-product of monazite mining.

The Director of the Imperial Institute will be glad to give any further information to inquirers who are interested in the utilization of refractory materials from sources within the British Empire.

SILICA AS A REFRACTORY MATERIAL.

Mr. Cosmo Johns, M.I.Mech.E., F.G.S. (Sheffield), read a Paper on "Silica as a Refractory Material."

Introduction.—Silica as a refractory material finds its most extensive application in the construction of furnaces employed for the manufacture of steel by the acid and basic open-hearth processes. In this short Paper it is only proposed to discuss some of the problems that arise in that particular application of one or other of its mineral forms. Quartz, which is the silica mineral used, occurs in some abundance, and in a state of comparative purity, near most of the coalfields which nourish the steel industry in this country. In the open-hearth steel process the silica is used as sand to form and repair the hearth in acid furnaces, and as silica brick for furnace construction in both acid and basic processes. Silica bricks have been made for more than a century, but even to-day the art is probably far in advance of the science of the industry.

The researches of Day and his fellow-workers at the Geophysical Laboratory, Washington, on the nitrogen thermometer have laid the foundation for accurate temperature-determinations in the critical range of the silica minerals, while the valuable papers* on the binary and ternary systems of $\text{SiO}_2 - \text{CaO}$ -- $\text{Al}_2\text{O}_3 - \text{MgO}$ which have appeared since 1905 must form the basis of any future work. Among the later papers an important discussion by Fenner of the "Stability Relations of the Silica Minerals" † is valuable in that it revises some of the conclusions of Day and Shepherd and explains many of the anomalies noticed by them. The cruder experimental methods of the earlier workers on refractories leave so much uncertainty as to the temperatures they record and the identification of the minerals obtained, that only confusion would result from quoting their results if they were given the status of those obtained at Washington.

Service Conditions.—Fenner found the melting-point of cristobalite to be $1,625^\circ$, but pointed out that by melting-point he meant deorientation of crystalline structure. He noticed that the amorphous silica retained considerable stiffness much above $1,625^\circ$. It is extremely fortunate that silica should possess a wide melting range ‡ instead of a melting-point. It is difficult to determine the temperature of the walls of an open-hearth furnace, but a number of attempts with an optical pyrometer suggests $1,650^\circ \pm 50^\circ$ as a probable value. The temperature of the flame is in the neighbourhood of

* A list of papers, together with a revision of the melting-points determined in that laboratory, appeared in *Am. Jour. Science*, vol. xxi., p. 341 *et seq.*

† *Am. Jour. Science*, vol. xxxvi., p. 331 *et seq.*, 1913.

‡ Bowen, *Am. Jour. Science*, vol. xxxviii., p. 213, 1914, found the melting-point of cristobalite to be not only higher than $1,625^\circ$, but higher than Endell and Riecke's value of $1,685^\circ$.

1,800°, and the brightness of the flame as seen with the walls or blocks as a background is a measure of their temperature difference. The bricks carrying the greatest load are only heated to this high temperature on their face, so that the margin of safety is greater than would at first be imagined.

An examination of the fractured surface of a brick that has been exposed to the furnace atmosphere for a long period reveals the fact that the portion next to the interior of the furnace is much darker, and on investigation proves to be much denser. The brick is in the condition known to the furnace-man as "seasoned." It is more refractory, and withstands temperature variations without fracture. If the dark portion be finely crushed, magnetic oxide of iron up to 15 per cent. by weight can be removed with the aid of a magnet. Magnetic oxide of iron is the stable oxide at high temperatures, and does not combine with silica, nor does it form a solid solution at furnace temperatures.

It is noteworthy that the presence of such a quantity of magnetic oxide of iron should be accompanied by improved quality in the brick. Probably it merely "indicates" a long annealing at high temperature, and that this annealing has favoured the changes that had not been completed during the manufacture of the brick. Possibly, however, the magnetite is not a passive constituent.

It is rarely that quartzites used for silica-brick manufacture contain much oxide of iron, and ferruginous quartzites are not sought for as raw material for the industry. In Japan* a ferruginous quartzite containing 4.5 per cent. of ferric oxide was tried, with the unexpected result that the brick made, despite its unattractive colour, was rather more refractory than the usual type of silica brick, and withstood variations of temperature much better. It would be interesting to try the effect of adding finely divided magnetic oxide of iron to the orthodox mixture. The results would not be strictly comparable, for the oxide would only occur in the matrix, while in the Japanese experiment it was disseminated through the quartzite. They would, however, approximate to the seasoned brick referred to above. Bricks containing oxide of iron should be burnt in an oxidizing atmosphere, to avoid the formation of the fusible ferrous silicate.

It is only in the portion of the furnace exposed to an oxidizing atmosphere that the presence of magnetic oxide of iron in the "seasoned" brick is not only not detrimental but possibly advantageous. In the gas uptakes, where during alternate reversals the incoming gaseous fuel at a high temperature is in contact with the brick, corrosion due to the formation of ferrous silicate takes place. Fine-textured bricks seem to be the most rapidly attacked, and the larger fragments of silica are the last to yield.

The Silica Brick.—The silica brick consists of crushed quartzite of variable purity, mixed with a small percentage of lime, moulded into the desired form, dried, and then, by suitable heat treatment, converted into a mineral complex, which when used for furnace construction possesses certain desirable properties. These properties are (1) ability to stand temperature changes without cracking or disintegration; (2) refractoriness at the highest temperature employed in the furnace; (3) resistance to the attack of the combustion and reaction products found in the furnace atmosphere; (4) a regular and not excessive coefficient of expansion.

There is evidence that variability in these properties is not altogether due to differences in the composition of the raw material used or in their proportions, though they are not excluded from the possible causes. It is certain, however, that differences in the size of the quartz fragments used would

* Communicated to author by Captain Noda, Imperial Japanese Navy.

have important consequences, and the nature of the heat treatment must be a controlling factor in determining the particular mineral complex formed.

The brick in its simplest aspect consists of fragments of silica, in one of its forms stable at high temperature, as an aggregate, with a matrix of lime silicate. The lime silicate is less refractory than the cristobalite, and its presence is a necessary evil.

Texture.—The concentration of the lime silicate will depend upon the extent of surface of the original quartzite fragments in contact with the lime used and the thermal history of the brick, and with varying concentration one can expect a variation in properties and an explanation of the marked differences in behaviour during service of various bricks.

As the function of the lime is to bind the quartzite fragments together, the problem is one of grain-size* and packing. Now the surface exposed varies inversely with the diameter of the grain, so that large grains are suggested; but grains of uniform size give the maximum of void space, hence the desirability of using more than one size of grain. A continental works making a good brick employed two sizes, 7 mm. and 3 mm., with the fine material that resulted from the crushing as the third size. This agrees with the sizes employed by some other makers, but departures from this rule occur, and it would be desirable to make careful experiments with bricks containing varied sizes of quartzite fragments and varying ratio of sizes, with a view to correlating texture and behaviour under furnace conditions. The data required are measurable, and when once determined would clear the way for the solution of the next problem.

Heat Treatment.—According to Fenner, the principal inversions of silica are—

α quartz \longrightarrow β quartz, 575° .

β quartz \longrightarrow tridymite, $870^{\circ} \pm 10^{\circ}$.

Tridymite \longrightarrow cristobalite, $1,470^{\circ} \pm 10^{\circ}$.

This refers to pure material, and a flux had to be used at times. But the relations are by no means simple, and from certain melts unstable phases appeared. Now, few if any minerals occur in a state of purity in nature, and certainly the raw materials of the silica-brick industry are not pure, nor perhaps is it desirable that they should be. It follows that the utility of attempting to predict the occurrence of definite phases in such a mineral complex as the silica brick at certain temperatures is questionable. Further, a petrological examination of the cold brick after burning or after use under furnace conditions could not be expected to throw much light on its constitution at high temperatures. It would only be by quenching fragments from furnace temperatures that such information could be obtained. It can reasonably be expected that ultimately, after texture and heat treatment have been fixed, a petrological examination of the brick in the state it leaves the maker would enable one to predict with some success its behaviour in the open-hearth furnace.

If, however, after the correct texture had been determined, a careful investigation of the effects of varying heat treatment during burning were made by correlating the time-temperature curve with behaviour in service under furnace conditions, most useful data would be obtained. In the course of that work, the effect of oxidizing and reducing atmospheres and the permissible range of temperature during burning could be determined. When

* The influence of grain-size and its relation to the matrix has been often discussed in reference to asphalt pavements, concrete, coal briquets, etc. A useful discussion of the principles involved is given by Mills, *Bull.* 343 *U.S. Geological Survey*, Washington, 1908.

the most suitable conditions had been determined, it would remain for the manufacturer to translate them into terms of successful practice. After texture and heat treatment had been expressed in terms of precision, the value of various bonds and the use of catalysts would be useful subjects of research. Art has probably partly anticipated science in this direction.

Silica Sand.—Except for drying, silica sand is used as received. It is necessary that the grains should not be too small, for the banks of the hearth are formed by the sand assuming its normal angle of rest, and this, at furnace temperatures, when many of the quartz grains have passed the α - β inversion point, is not so easily effected as when the sand was at ordinary temperatures. It is also necessary that the sand should possess a certain degree of refractoriness. It must frit in a reasonable time when thrown into the hot furnace at ordinary working temperatures, and yet should not become viscous during the prolonged melting operations. It is possible that the melting-point of quartz, as distinct from that of cristobalite, is often achieved when silica sand, in the presence of small amounts of impurities, is used in this way. Extreme purity in the sand is of no advantage when it is used by itself. The permissible range of impurities can only be suggested tentatively. Al_2O_3 up to 2 per cent., and probably higher; Fe_2O_3 up to 0.5 per cent.; CaO , 0.5 per cent.; MgO , 0.5 per cent.; Na_2O , 0.15 per cent.; K_2O , 0.15 per cent. would be admissible if only one impurity were present; if more than one are present the amounts would be reduced proportionately.

The analyses of various sands which are tabulated below (p. 85) indicate ranges of impurities found compatible with useful service.

TABLE.

*Analyses of Refractory Sands.**

Date of Analysis :	Sept. 11, 1907.	April 24, 1915.	April 24, 1915.	April 24, 1915.	Feb. 24, 1916.	April 24, 1915.	May 17, 1916.	Mar. 25, 1916.	Nov. 20, 1916.	Feb. 11, 1916.	Nov. 20, 1916.	Oct. 16, 1914.	Authority.
Locality :	Belgium.	Belgium.	Holland.	Rouen.	Aylesbury.	Leighton Buzzard (ordinary).	Leighton Buzzard (double-washed).	Lynn (washed).	Malton (unwashed).	Yarmouth.			J. H. Huxley, A.R.S.M., F.I.C.
Moisture and organic matter													
SiO ₂ ...	24	20	12	20	20	20	20	35	80	40	65	170	
Al ₂ O ₃ ...	99'10	98'15	97'78	99'45	99'35	96'00	99'50	99'90	96'20	98'45	91'85	94'40	
Fe ₂ O ₃ ...	36	70	1'70	15	60	84	04	58	1'58	64	5'80	3'66	
CaO ...	24	30	20	15	nil	2'86	43	18	43	30	trace	29	
MgO ...	nil	25	trace	nil	nil	trace	nil	nil	40	20	60	10	
Alk. oxides ...	07	nil	nil	nil	nil	nil	nil	nil	50	nil	1'00	nil	
	nil	20	25	nil	nil	20	nil	nil	nil	16	nil	trace	
Total ...	100'01	99'80	100'05	99'95	100'15	100'10	100'17	100'01	99'91	100'15	99'90	100'15	
	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.	L.	

* By permission of Vickers Ltd.

The following remarks are based on the experience of the author under conditions which do not necessarily apply everywhere :—

A, B, G, H. Have been used successfully.

C, J. Were used, but represent approach to maximum impurities permitted.

D. Used to increase refractoriness of C and J.

E. Too fine in grain.

F. Well spoken of in some works.

K, L. Not promising enough for trial.

I. Not yet available for trial. Should improve with washing.

ON THE MANUFACTURE OF REFRACTORY MATERIALS

Mr. Albert Cliff (Stamford) spoke "On the Manufacture of Refractory Materials," putting forward in a general way the makers' point of view.

My function at this meeting is to say a few things from the makers' point of view, which could not find expression at a better time or on a more fitting occasion.

I feel sure I correctly interpret the feelings of our fire-clay and silica manufacturers—especially those associated with the Society of British Gas Industries—when I say how much we appreciate your growing interest in refractory products. We owe a debt to several gentlemen who are here to-day. We owe most, perhaps, to the quiet personality of Dr. Mellor, who has already done a large body of enduring work, and who is the special object of our goodwill.

So far as I know, the bulk of the British makers of refractory articles have restricted manufacture almost wholly to the output of retorts, blocks, and bricks in fire-clay or silica. A good deal of controversy has in recent years gathered round the making of retorts used for the manufacture of town gas. Although the controversy referred to is now a matter of history, a few general remarks on the subject of retorts may perhaps be usefully made here. One of the best means of effecting the elimination of expansion and contraction, and incidentally effecting an economy, would be secured by the return of old material which has done service over a period of years at varying temperatures back to the seat of manufacture. The material is no worse for discoloration by carbon, which would burn off on re-manufacture. Partially fused or slagged pieces would require to be kept out. Although there is a cleavage of opinion among gas engineers as to which is the better—hand-made or machine-made retorts—it may be put on record that this country pioneered the manufacture of retorts by machinery.

Makers have hitherto mostly concerned themselves with the supply of acid refractories. But in the basic and neutral groups there is an inviting prospect for the application of manufacturing skill. There are difficulties peculiar to the present time. There is not the same abundant importation of minerals as in normal times. Cost is also a deterrent just now. These temporary difficulties we ourselves are endeavouring to surmount by fastening working surfaces of chromite, magnesite, or other minerals calculated to secure furnace linings against corrosion or attack from various causes on ordinary fire or silica bricks. Like most things in clay, it opens out more complications. It is a variation of the facing or engobing of bricks, of which most of us have had experience. I have brought a few samples down for your inspection, and I may say we have already had considerable encouragement.

What are the practical uses of this meeting? We are here to learn wisdom from the past, and it should be still more easy to learn wisdom from current events. We know full well that the whole fabric of our ideas needs searching reform. To set about this is better than wailing about the past. There has never been a time since brickmaking began when an industry was more aflame with earnest longing for improvement, and while it can never go back, rolling along the old channels, everything that can be done to promote a better order should be done now.

Work of great urgency awaits both the chemist and the craft in making an organized investigation into the commercial value of chromite, magnesite, graphite, and other minerals reported as abundant in the Colonies. I want to say with respect that laboratory tests which could speedily be carried out are not enough. Years of patient observation are frequently necessary in order to establish the quality and fitness of such materials under practical conditions.

If, too, the industry is to occupy its rightful position, it will have to be founded on an improved education; and although statesmen may be slow to come to our aid, still there is room for action. The Faraday gift was never more needed in this country than now. If we could secure men of science to communicate more freely facts and principles to the youth of the fire-clay districts, speaking to them about and exhibiting to them gases and materials, I am certain that at small cost to the mind you would render invaluable aid. It is not to be forgotten that we are on the eve of the greatest industrial opportunity this country has ever had, and we are in less danger of wasting it if chemists of the right sort would go down occasionally to the leading fire-clay centres and, supported with all the influence which employers can bring to bear, speak with appropriate clearness to the rising race. In the past they have been left sadly too much to their own unguided intuition, when steps should have been taken in some such way to rouse them to reflection on their task. It is almost unnecessary to suggest that there is embraced in some of the commonest materials, such, for example, as "a piece of silica," a story as arresting to the vulgar as anything inside a picture house. I may be forgiven if I bluntly tell of an incident within my own knowledge which occurred at a works in Yorkshire County. Owing to the shortage of prepared fire-clay, an employee was called upon to leave the works before the appointed time. "What is tha going hoam for, Bill?" shouted a fellow-worker; to which Bill subjunctively replied, "Becoss thear is noa muck." There is coarse humour in this, but we dare not in the coming time perpetuate the unbroken night in which the majority of our workers have been reared. Our own hard-crusted indifference, which is the real criminal, must be broken up. If the spirit of the times is not sufficient, then the man who is powerful enough to do that will perform a national service. We greatly need more first-class minds given up wholly to the chemistry of the trade, but it is also obvious that these must have an intimate union with the minds of the workers, and I feel that a good deal is to be expected by accelerating a rise of specialized intelligence among clayworkers.

I believe the makers of refractory materials are alive to the responsibilities of the hour and preparing to be equal to all demands. We on our side expect much from our scientific friends. Hitherto the growth of knowledge, particularly in this branch, has been painfully slow. For thirty years I have personally endeavoured to absorb all the available information on clays, and although I have never been set down as a particularly sluggish student, I am much more distinguished for what I don't know than for what I do know about the endless complexities of this subject.

I sometimes think something like this was in the mind of the writer when he said—

“Were man to live coeval with the sun,
The patriarch pupil would be learning still,
And, dying, leave his lesson half unlearnt.”

However, it is peculiarly in the power of this meeting to speed up the good work, and coming here to-day will have been well worth while if it bears witness to the unity with which we shall carry on in the future.

THE CLASSIFICATION OF REFRACTORY MATERIALS.

Mr. E. P. Page (Sheffield) read a Paper on "The Classification of Refractory Materials."

This Paper is confined in the main to the materials used in the heavy industries, and I have not attempted to deal in detail with the refractory materials used in the lesser known paths of metallurgical practice. To cover the whole field of refractory materials and their application in all branches of industry would be beyond the range of accomplishment in any single Paper.

The collection and tabulation of facts is a laborious task, since much of the information is only to be obtained by association with those who are engaged in industrial practice—further, the science of refractory materials is in its infancy, and much of that which is considered fact requires verification.

The usual method of classifying refractory materials has been to divide them into three classes, viz. acid, basic, and neutral, according to their chemical composition and their behaviour towards each other, and acid or basic compounds brought into contact with them, under such conditions as are favourable for reaction to take place. The classification is somewhat arbitrary, because a clay such as china clay might be expected from its chemical composition to be a neutral material; experience, however, shows that such is not the case, and it is customary to include all refractory clays in the acid class.

The essential property of any material claimed to be refractory is stability at temperatures to which it is exposed, with sufficient reserve of stability to resist chemical and mechanical influences externally applied. The first quality is a question of pure refractoriness, the second is one of refractoriness plus skill in application.

Further, since purely basic or purely acid conditions seldom exist, the successful issue is generally the result of compromise, a certain degree of refractoriness *per se* being sacrificed in favour of increased refractoriness against other influences.

Materials belonging to the "acid" class are always used where it is a case of refractoriness towards heat, because they are widely distributed and comparatively low in first cost, and lend themselves readily to adaptation for particular purposes. Suitable "basic" and "neutral" materials, on the other hand, are not so widely distributed and possess in many instances inherent properties which render them difficult of application.

I propose to follow the usual method of dividing all refractory materials into three classes, viz. acid, basic, and neutral, and to indicate the application of the various materials in each class.

Acid Materials.

Silicious materials, with a content of SiO_2 ranging from 100 per cent. to 80 per cent. (below 80 per cent. would be included as a clay), embracing quartz, quartzites—sandstones—sand.

The purest forms of silica are used in the manufacture of quartz glass, which is worked up into a variety of articles used mainly in chemical operations.

The less pure forms of silicious rocks (quartzites, ganister, etc.) are used in the manufacture of "silica bricks," and in the preparation of material which is used as a more or less plastic mortar and rammed into position in the raw state.

The best silica rocks for these purposes average from 95 to 98 per cent. SiO_2 , and soften at about 1,800 to 1,850° C. Such rock is widely distributed and exists in many varieties, most of which can be used in the ground state as a prepared mass, and few of which have so far been used successfully in the manufacture of first-class silica bricks and blocks. The quality of a silica brick depends more on the physical and mechanical properties of the stone or rock than on chemical composition. All silicious materials expand on heating, and some expand to an extent which renders them useless in the manufacture of silica bricks. The problem before the silica brick manufacturer is to secure toughness and increasing density in use, and that the problem is not insoluble is proved by the specimen brick shown.

Large quantities of silica are used in the form of sand for forming the hearths of open-hearth furnaces and in iron and steel foundries.

Refractory Clay.

This material is also widely distributed and of great variety. Refractoriness generally varies directly with the content of alumina. The most refractory clay corresponds to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - (2\text{H}_2\text{O})$, which softens at about cone 35–36, any increase in the ratio of silica to alumina reducing the refractoriness. Clays corresponding to this composition are scarce, the most abundant being the china clays. The clays obtained from the coal measures contain less alumina, and with one or two exceptions are less refractory. There is another class of refractory clays generally known as "ball" clays, which are generally more silicious than china clay, and vary in refractoriness accordingly.

The chemical composition gives no clue on which to base any conception as to its physical properties—

	1		2	
	China Clay.		Grunstadt Clay.	
Silica	54·65	...	47·69
Alumina	44·51	...	38·15
Oxide of iron	...	·22	...	·077
Lime	·13	...	·21
Magnesia	·09	...	·12
Potash	·34	...	·26

Formule.

No. 1. $\text{Al}_2\text{O}_3 \cdot 2·09 \text{SiO}_2 \cdot 0·027 \text{RO}$; refractory cone, 36.

No. 2. $\text{Al}_2\text{O}_3 \cdot 2·125 \text{SiO}_2 \cdot 0·0775 \text{RO}$; refractory cone, 35.

In composition these two clays are very similar, but the result of heating to approximately 1,300° C. is to reduce No. 2 to a dense vitreous structure, whilst No. 1 will be found to be strongly absorbent and porous. In the raw

state No. 1 is not plastic and has no bonding power, whilst No. 2 is plastic and has great bonding power.

This comparison of two clays of similar composition and unlike physical properties will give an idea of the problems which the manufacturer has to solve. It is sometimes necessary to construct a vessel which will keep its shape at high temperatures, and at the same time withstand the solvent action of molten slag or glass. Now, however perfectly refractory the clay may be as regards heat, it is useless if it absorbs the slag or glass, because this immediately reduces the refractoriness towards heat. Hence, as already mentioned, it is necessary to compromise between the two qualities.

Large quantities of "acid" materials are used in the raw state. Silica is ground, sometimes with clay and sometimes without, to a semi-plastic mass, and used for lining steel converters, ironfounders' cupolas, steel ladles, etc.; for this purpose inferior kinds of quartzites are used, according to the resources of the district. In Sheffield the crucible pot furnaces are formed by ramming ground ganister round a plug or core.

Converters are lined with silica brick, and all wear is made up with ganister, which is "daubed" on.

The iron and steel founder uses acid materials for making moulds. Sands suitable for iron castings are plentiful and the ironfounder has little difficulty in getting supplies. The demands made on moulding materials in the steel foundry are very much more exacting than is the case with iron, and much ingenuity is used by the steelfounder to adapt his moulding materials to meet his needs. The size and shape of the casting, the class of steel, and many other factors have to be considered.

Sand is used very largely for small and medium-sized steel castings. "Composition" is also used; this consists of a mixture of old crucible pots, ganister, calcined and raw, fire-clay, blacklead, and sand. Every foundry has its own mixings and recipes. The essential property of a moulding material is sufficient "bond" to enable it to keep its shape, which is often very intricate, and when dry it must be firm enough to stand the flow of the metal, and finally, especially in the case of "cores," it must break up and leave the casting clear.

The problems which arise in connection with moulding materials are quite distinct from those arising in brick-making, and provide sufficient matter for research on their own account.

Basic Materials—Magnesite : Dolomite : Alumina.

Magnesite is one of the most useful of the basic materials. It can be used in the form of bricks and special shapes, and also as a rammed mass for furnace bottoms, etc.

It is highly refractory, but possesses the disadvantage of being a good conductor of heat. It is obtained in a form suitable for use in metallurgical operations by burning the naturally occurring magnesium carbonate rock at very high temperatures; not only must all traces of CO_2 be driven off, but the oxide resulting from the first stage of calcination must be heated until it has attained its maximum density. In the discussion on a paper read before this Society by E. Kilburn Scott in 1905 it was stated that as the result of heat the density of magnesium oxide varied as follows:—

Heated to 350° C.	3'193
„ dull red	3'248
„ white heat	3'670
Fused in electric arc	3'684

and Dr. Hutton goes on to say that "fused magnesia, as also fused alumina, behaves like fused quartz in being able to withstand somewhat sudden changes of temperature without fracture, although, of course, the behaviour varies in degree."

Bricks made of magnesia, shrunk at the highest temperature short of the electric arc, are in many respects unsatisfactory, being unstable at moderately high temperatures; they are unsuitable for the construction of arches, and even if used in plain furnace walling they disintegrate. They are used in large numbers in the bottoms of Siemens basic furnaces underneath the dolomite hearth, and are for this particular purpose quite satisfactory.

J. Horhager* gives some particulars of magnesite deposits in Austria and Greece, and states that the crystalline varieties of stone found in Austria, containing 2 to 8 per cent. of Fe_2O_3 , are the most suitable for use in making dead burnt magnesite; though he states that very satisfactory material is made in England from the purer amorphous form of magnesite obtained from Eubœa. He mentions the following figures as representing the ideal composition:—

Minimum,	83	per cent.	MgO.
"	3	"	Fe_2O_3 .
Maximum,	5	"	CaO.
"	2	"	Al_2O_3 .
"	5	"	SiO_2 .

In America and on the continent of Europe magnesite is used for ramming up the furnace bottoms of both basic open-hearth and electric furnaces, on account of its refractoriness towards basic slags and metallic oxides; in Great Britain, however, dolomite is found to be satisfactory.

Dolomite.—This material, as used, is the product obtained after burning magnesian limestone at a very high temperature until it has not only lost all the CO_2 , but has attained great density; its refractoriness is affected by the content of silica and iron and the ratio of the two latter to each other.

Shrunk dolomite hydrates at a rate dependent on atmospheric conditions, and is always used as "fresh" as possible. It is very refractory towards heat, basic slags, and metallic oxides, though at the temperature of the open-hearth furnace it is "friable."

For furnace bottoms it is crushed, mixed with dehydrated tar, put on in thin layers and rammed with hot rammers to the required shape. For lining basic Bessemer converters the material is crushed, and after mixing with tar is pressed in hydraulic presses into the form of blocks.

Dolomite has also been made into bricks of a density equal to magnesite bricks; the temperature at which the bricks are burnt must, however, be sufficiently high to sinter the particles together.

The combination of dolomite and tar under the influence of heat gives much better results than magnesite and tar. The tar oils and acids react with the lime, and after the volatile constituents of the tar have been driven off a compact homogeneous mass of dolomite and carbon is left.

Alumina.—This is a valuable refractory material, but the price at which it is obtainable is against any very extensive use. For very special purposes, and where first cost is not a consideration, it can be mixed with plastic clays in any proportion, and will raise the refractoriness of the clay to a degree depending on the amount of the alumina added.

* *Stahl und Eisen*, 24, 1911.

- *Neutral Materials.—Chrome : Carbon : Zirconia : Bauxite.*

Chrome is a very useful refractory, under certain conditions. It can be made into bricks and special shapes or used in the lump and ground condition. In the early days of the basic steel process chrome bricks were always used as an insulating material between the magnesite bricks in the bottom and the silica bricks of the side walls. This practice is not now generally followed, because it has been found that magnesite and silica bricks can be laid in contact with each other.

Chrome bricks are difficult to manufacture, inasmuch as the material has a low softening-point, and the bricks if subjected to any weight in the kiln collapse. Ground chrome is an exceedingly useful material. It can be used as a mortar in contact with dolomite, to repair a dolomite hearth. Electric furnace operators use it extensively for all sorts of purposes.

Bauxite.—This is a naturally occurring hydrate of alumina always mixed with some clay matter or hydrated oxide of iron. The content of water in the raw material varies from 5 or 6 per cent. to 30 per cent. Before it can be used it requires shrinking at very high temperatures, and some varieties require repeated burning before all the shrinkage is taken out. The best material is that which has been fused in the electric furnace. A fused bauxite known as alundum has been tried for the roofs of electric furnaces ; it was found, however, that the vapours of lime and magnesia attacked the bricks and caused them to fail.

Carbon.—This is a useful refractory material, but it cannot of course be used under oxidizing conditions. Carbon blocks were, I believe, imported to line the hearth of a blast furnace in the north-eastern district. The result of the experiment will be of much interest.

Zirconia.—This material has been the subject of investigation, and experiments to determine its value in metallurgical operations are in progress.

DISCUSSION.

At this point the **President** thought it advisable, as the hour was getting late, to discontinue for the time being the reading of the set Papers, and he called upon Mr. W. J. Jones to open the General Discussion on the Papers they had already heard.

Mr. W. J. Jones (Ministry of Munitions) : I did not know I was to speak at a meeting of the Faraday Society, especially as I have not a sufficiently technically trained mind, but it might interest you if I told you a little of the experiences which the Steel Production Department of the Ministry of Munitions have gone through. I have listened with much interest to the papers read this evening ; one thing which comes forcibly to my mind is that after listening to Professor Fearnside's paper and Mr. Johns' paper I think these indicate the necessity of a more close co-ordination between the scientific and manufacturing sides of steel production. Professor Fearnside's paper was of the deepest interest, and it was entirely different in its treatment and in its matter from that of Mr. Johns, but I think it shows that this country is at present interesting itself and doing its utmost to improve its steel production capacity, and that it will be a good thing if the laboratory side of the industry could co-ordinate more closely with the silica-brick making side of the industry and with the steel producing side of the industry. The steel industry can quite well afford to set up some organization by which the three aspects could be brought more closely together, so that the producers of refractory materials could have assistance to enable them to more rapidly produce the perfect brick which is required in the steel-melting furnace. I do not think the steel industry ever sufficiently regarded the importance of silica bricks in furnace construction until this war. They were always in a position to get as many silica bricks as they required, but the necessity for largely increasing the output of steel at very short notice has brought home very forcibly to the minds of all steel-makers the great part that refractory materials play in connection with furnace construction, and incidentally the output of steel in this country. I should like to say how well I have been supported since I took over the Department of Refractory Materials at the Ministry by the whole of the manufacturers of this country. It was a physical impossibility for them to meet as quickly as was necessary the extraordinarily increased demand for silica bricks, due to the large number of furnaces that were put into operation. This heavy demand tended in part to reduce the quality of the brick on the one side, and on the other side, the furnaces have been worked at a much higher pressure than normally, and consequently the length of life of the bricks has been largely reduced. I have also noticed whilst I have been at the Ministry that the silica brick that is produced has to bear the sins of a good many other people. I have found that bricks which are produced by the same firm at the same time have been sent to different steelworks, and whereas in one case I have had complaints that they will only last for about twenty casts from the furnace, in other cases I have had no complaints at all and renewals have not been required for perhaps three or four months, so that that again shows the necessity for this closer co-operation which I advocate not only in regard to the manufacture of refractory materials, but it also shows the necessity and desirability of scientific knowledge being brought to bear on the design of the furnaces themselves, and on the working of the furnaces, because I have seen that some furnaces come down through

improper working. Then with regard to bye-product recovery coke ovens for the production of metallurgical coke, I think there also there is a great field for science to go hand in hand with practice, because coke-oven brick makers do not possess the knowledge which is necessary to enable them so to vary the composition of their quartzite bricks which are used in the walls of coke ovens as to meet the varying conditions that they have to comply with in regard to the different qualities and the chemical compositions of the coals which have to be coked. I would urge that if we are to be an important steel-producing country, and if we are to go forward and secure that trade from our enemies, which is the great desideratum of us all, there should be a closer co-ordination between the laboratory, the steelworks, and the refractory materials works.

Mr. A. McDougall Duckham (Ministry of Munitions): Since I have been at the Ministry I have felt how much we rely on refractory bricks. Experience shows that we have the finest materials in this country, and we certainly have the brains to say how the material should be treated, mixed, and burned; all we want is to obtain the co-ordination just referred to, and it seems to me that that co-ordination is very easy to obtain; it is chiefly a question of, say, dropping our internal insularity and coming together for an end. Another factor is necessary, a thing which most of us have got a certain amount of, that is money, and if the necessary funds are put at the disposal of the scientists it would enable them to work for both manufacturers and users, and would give us the finest results obtainable. I am certain that with the means, the brains, and the materials co-ordinated we shall very easily hold our own and do what we expect ourselves to do.

Mr. F. W. Harbord, called upon by the President, said: If you will allow me, I will defer any remarks I have to make until a later meeting, if you have one, or I will put them in writing. I see there are many gentlemen here who have come long distances, and I would rather give them an opportunity to speak.

(*Communicated November 26, 1916*): It was with the greatest pleasure that I listened to the papers on the important subject of refractories. I had hoped that during the discussion some of our practical brickmakers would have expressed their views on some of the very important practical questions which have arisen largely as a result of the war.

Before the war the manufacture of magnesite bricks was carried on to a very limited extent in this country, and we had to rely almost entirely on the bricks imported from Austria. Since the war we have established what may almost be regarded as a new industry, and have not only supplied our own wants, but very largely those of our Allies. Many of these bricks are of excellent quality, but from information I have received indirectly I am afraid, in many cases, they are not equal to the Austrian bricks. How far this is due to a difference in the analysis of the Austrian magnesite as compared with the Grecian magnesite, from which practically all our bricks are made, or how far it is due to slight differences in manufacture, such as methods of burning, pressing, fineness of grinding, etc., it is very difficult to say, but these are questions which should, as soon as possible, be tackled by our magnesite brick manufacturers, as after the war, if we are to retain this industry in this country, we must make a brick which is equal to, if not superior to, that which can be obtained from Austria.

Another brick which was largely imported from Germany before the war was the brick used in coke ovens, and here again we had considerable difficulty in the early days of the war in obtaining bricks suitable for the purpose.

The question of contraction and expansion under the particular conditions which exist in the coke ovens, and the great importance of obtaining a brick which on cooling down shall not unduly contract, is of vital importance, and it behoves our brickmakers to investigate most carefully, both from a practical and scientific point of view, how to produce a brick which should be equal in every respect to that which was imported from Germany.

I am glad to say that some manufacturers have succeeded in making a brick which is very nearly, if not, equal to the German brick, but some of the bricks which have been put into coke ovens have behaved very badly and are now causing most serious trouble.

The importance of a satisfactory brick for coke ovens does not need emphasizing to any practical man, for if an oven has to be shut off for repairs in six months instead of eighteen, the reduction of output and indirect losses are obvious to everybody.

Another point I would like to call the attention of practical brickmakers to is the supplying of a satisfactory refractory, both as regards bricks and clay, for retorts for zinc-smelting furnaces.

We hope, after the war, that the zinc industry in this country will be established on a firm and sound basis, and that instead of having to import, as at present, two-thirds of the spelter we use, we may, to a large extent, become self-supporting.

If, however, we are to produce spelter on a large scale in this country it is absolutely necessary that we should have available satisfactory refractory materials, as indirectly the cost of zinc smelting very greatly depends upon having a class of firebrick and clay which will resist both the high temperature and fluxing action of the ores which have to be treated.

I am not a brickmaker and claim very little detail knowledge of either the theoretical or practical side of brick manufacture, but I am fully convinced that if these problems are to be satisfactorily solved in a reasonable time it can only be done by co-operation between practical brickmakers and scientific experts who have specialized in refractory materials.

If these two will only work together, each assisting and supplementing the other, in a very short time, with the natural resources we have in the way of raw materials, I believe we shall be able to hold our own with any country in the world.

Dr. W. Rosenhain, F.R.S. : I shall not attempt to detain the meeting very long to-night, but there are two main points with which I wish to deal quite briefly. The first of these relates to the general subject of what may be termed "special" refractories, capable of resisting higher temperatures than those normally encountered in the open-hearth steel furnace. A review of the history of metallurgy in modern times at once affords the indication that metallurgical progress has generally been accompanied, and even conditioned, by the use of increasingly high temperatures, and there is every indication that future progress will take the same direction. There can be no doubt that the importance of the electric furnace as a metallurgical tool is becoming steadily greater. It may be that the great bulk productions of our staple metallurgical industries—both iron and steel and non-ferrous—will continue to be produced by fuel-fired furnaces, yet even now the special steel industry is becoming dependent upon ferro-alloys produced in the electric furnace. With this view of the future in mind, I am anxious to press upon the attention of those interested in refractories the need for the exhaustive study of those "special" refractories which are capable of resisting the very high temperatures of the electric furnace, frequently considerably above 2,000° C. In this matter at the present moment America appears to lead the way,

no doubt owing to the extent to which that branch of industry is favoured in America by natural water-power. But even if we should find it difficult to compete with the electric-furnace products made by the aid of American water-power, it is none the less of most extreme importance that we should study this branch of the subject of refractories. There is in this branch, even more than in others, a very wide field for fruitful research. The American products, such as carborundum, alundum, Acheson graphite, etc., are interesting and valuable, but we may be perfectly certain that they have not yet exhausted the resources of nature. I think that it would be most desirable if one or more of our scientific institutions made this line of work peculiarly their own, so that we might develop an indigenous knowledge of materials of this class. This would be well worth doing, even if we remained interested in such materials merely as users, and we certainly shall have to use them extensively; but I do not think that we need remain dependent upon America or any other country in this matter. Even if electric power should cost rather more, the real source of success lies more in real knowledge and in technical efficiency based on such knowledge than on any other factor.

My next point relates specifically to one substance which has already been mentioned this evening, zirconia. This is certainly one of the special refractories to which I have just referred, and I am convinced that it has an important industrial future, although that future lies, perhaps, more in the manufactured purified zirconia than in the crude mineral product as it is at present obtained from Brazil. Unfortunately, this crude mineral does not frequently possess so satisfactory a composition as that quoted in his introductory address by the President. It is true that one form of the mineral (baddeleyite), which occurs in glassy lumps or nodules, does contain over 90 per cent. of zirconia, but unfortunately this relatively pure material is not very abundant. The more abundant form contains a very much smaller proportion of the oxide. The chemical analysis of a sample taken from a ton of the crude mineral is as follows:—

Zirconia	74.72 per cent.
Silica	13.16 "
Titanium	1.0 "
Iron oxide	3.5 "
Magnesium oxide	1.6 "
Alumina	1.1 "
Lime	2.16 "

Material of that composition is far removed from pure zirconium oxide, and in its behaviour as regards refractoriness falls very far short of the pure oxide. Nevertheless, there are possibilities even in that crude material, which, if very finely powdered, has sufficient binding power to be formed into bricks by itself; it can also be made into bricks by the addition of a little refractory clay, such as china-clay, as binder, and in the latter case the bulk of the crude zirconia can be previously burnt at a high temperature and used as "grog." So far as laboratory tests go, such material resists a temperature well over 1,630° C. very successfully. At the same time it possesses other important advantages, such as very low thermal conductivity and considerable mechanical strength, properties which render it most valuable for the lining of furnaces. It must, however, be borne in mind that the exposure to a temperature above 1,630° C., just referred to, was continued for a relatively short time only, and it remains to be seen by actual furnace trials whether prolonged exposure, for days and weeks, brings about any gradual deterioration.

tion of the crude zirconia ware. Another difficulty in the use of this crude zirconia should perhaps be mentioned here—its very considerable shrinkage. This inevitably leads to the disintegration of bricks and linings, unless they or the grog from which they are prepared have been previously burnt at a temperature higher than that at which they are to be used. In the manufacture of bricks out of fire-clay or silica this is not usually done, and is not absolutely essential. If the burning temperature has been high enough to bring about the principal shrinkage of the material, then the subsequent shrinkage due to exposure to higher temperatures, although a disadvantage, is not absolutely disastrous. Zirconia, however, appears to continue shrinking approximately to the same extent with each further increment of temperature, and this property renders very high initial burning imperative. In this respect zirconia exhibits a similarity to magnesia, which also suffers from severe shrinkage troubles unless initially “dead burned” or preferably electrically shrunk or sintered.

A further difficulty in the case of zirconia arises from the great tendency which exists for the formation of zirconium carbide. The change from oxide to carbide involves volume changes which are very apt to lead to disintegration. This would probably not occur with a well-made zirconia brick in the atmosphere of an open-hearth steel furnace, but under extreme reducing conditions it might arise.

The refractory properties of zirconia can be enormously improved by purification. A small amount of such purification can be accomplished by simply washing the crude mineral with dilute sulphuric acid. By this means the content of iron oxide can be reduced from 3·5 per cent. to something like 1·5 per cent., and since the iron oxide is much the most violent fluxing agent among the impurities, this treatment materially improves the refractory qualities of the zirconia. The rest of the iron, however, and the other most serious impurity, the silica, cannot be removed in this way, and other more elaborate methods of treatment must be applied. In the course of the researches on the production of optical glass which are being carried on at the National Physical Laboratory, we have had to deal with zirconia because it promises to be of special value in that connection, and we have worked out what promises to be a comparatively cheap and simple method of purifying the crude zirconia mineral, either partially or, if desired, entirely. Samples of both products are on the table; the first contains only a trace of iron, but titania and alumina are still present; the second is really pure zirconium oxide. We have succeeded in melting this pure oxide in the electric arc, but it requires the highest temperatures obtainable with the arc to bring it to fusion. If the powder is made into a briquette and heated to well above 2,000° C. it shows no signs of fritting or cohering; it simply falls to pieces again. It can of course be made to cohere by depressing its extreme refractoriness by the addition of a suitable binder, such as a little clay, silica, or alumina.

Leaving these special materials, I would now like to refer briefly to a point which has been raised by previous contributions. This is the question of the extent to which a brick or other refractory body is capable of resisting sudden heating or cooling without undergoing fracture. I am assuming that the sudden heating or cooling in question is not the first heating or cooling, so that the body may be assumed to have previously undergone its full shrinkage or other internal changes leading to alterations of volume. In those circumstances the effects are due entirely to thermal expansion or contraction, and are capable of being calculated if the physical properties of the body are sufficiently known. The matter has been very fully studied

in the case of glass, where the property in question is sometimes described as "thermal endurance." The mechanism of fracture as a result of sudden heating is readily understood. Since heat is necessarily applied to such a body as a brick externally, the outer layers of the brick become hot, while the interior is still much colder. The thermal expansion of the outer layers is thus prevented and resisted by the adjacent colder inner layers, and a balance of forces is set up between them, as the result of which the inner layers are strained and stretched by a mechanical force derived from the outer layers, while the outer layers are compressed and thereby prevented from expanding to the full extent normal for their temperature. The amount of these balanced forces can be readily calculated when the coefficient of thermal expansion and the elastic modulus of the material are known. The higher both these constants are, the greater will be the stress set up by a given difference of temperature between adjacent layers. On the other hand, with given expansion and elastic coefficients, the stresses set up will be higher the greater the difference of temperature which arises between adjacent layers, i.e. the steeper the temperature gradient which exists in the material. But this again is dependent, for a given rate of heating, on the thermal conductivity, specific heat, and density of the material. Finally, whether rupture does or does not occur under given internal stresses thus developed will depend upon the tensile strength of the material. It is only the tensile strength which affects this question, because failure in materials of this kind always occurs in tension and not in compression; the compressive strength is always considerably higher than the tensile. It will be seen from the above that the "thermal endurance" or power to resist "heat shock" is a very complex matter, dependent upon a combination of a considerable number of physical factors. Where the aim is to produce a material of maximum resistance to sudden heating or cooling, the effect of any change of composition or structure on each of these physical properties must be carefully considered.

Professor T. Turner : It is a genuine pleasure to be here to-night and to listen to this important discussion, for I feel that few people realize the importance of the silicates to our country and to the world. We have not only the more fusible silicates, which yield glass with all its varied applications, but also the allied branches of clay manufacture to which reference has been made. We have, further, building bricks, the pottery and porcelain industry, and we have the refractories which we are specially considering to-night. After fuel and metals, I think we may claim that the silicates come next in order of usefulness and importance in the progress of the world. I was very pleased to hear the paper by Dr. Mellor, and the valuable scientific work that he has been doing in the Potteries Laboratory is well known. I was interested, as Director of Technical Instruction for Staffordshire, in the early development of that laboratory; and I am glad to see the work that is being done in connection with ceramics and with clays generally. I am also glad to know of the department of glass manufacture at the University of Sheffield. I had hoped we should have had a department dealing with that subject in my own University at Birmingham, but circumstances in connection with the war prevented that development, and gave the opportunity to Sheffield, where the new department is working under the direction of Dr. Turner, who was an old student at our University. I have not the pleasure of claiming him as a relative, but I feel sure the new department is destined to do extremely good work; and all those of us who are interested in the subject will be naturally only too glad to help Sheffield in this respect in any possible way. In the paper dealing with refractory materials by Major Bywater, reference is made to the effect of "weathering" a clay. This is an important pre-

liminary process with all ordinary fire-clay. The result is not merely the pulverizing of the clay and the separation of clay ironstone, but also the removal of potash, and that is one of the chief effects. This matter has been referred to, and dealt with at some length, by Mr. A. E. Tucker in his paper, "The Formation of and Analysis of Clays," which will be found in the *Journal of the Society of Chemical Industry* for 1910 (p. 467), and it might be interesting in connection with the bibliography that some reference to the work of Mr. Tucker should be added. Then Professor Fearnside referred to an important matter in connection with firebricks, when he said that what we found in the brick is not what we put in the brick, i.e. we find something different in the brick by the time it is baked from what we put into it. In other words, there have been important internal changes and alterations; chemical changes in the first place of a less definite character, and those are to an extent reversed as the temperature rises. The solubility of the silica, for example, changes as the temperature of heating the silicates increases. Excellent work in this direction was done by Professor Cobb. I do not know if he is here to speak upon it, but if not, I should like to make a special reference to his series of six papers in the *Journal of the Society of Chemical Industry* on "The Synthesis of a Glaze, Glass, or other Complex Silicate," commencing in January 1910. Those papers give us, I believe, what is the best information on this particular branch of the subject which we possess. In reference to the refractory material for coke ovens and similar apparatus, those of us who were present at the Brussels meeting of the Iron and Steel Institute in the autumn of 1913 had a paper presented to us on coke ovens in which Baron E. Coppée gave us some particulars of the firebrick manufactured for that particular type of oven. The Coppée Company were good enough to allow me to visit their laboratory and showed me the apparatus that they then had—I do not know what the Germans have done with it now—for measuring the changes of volume in a firebrick during the process of heating through a wide range of temperature. I have full particulars of that very delicate and beautiful piece of apparatus, with drawings; and an illustrated description will be found in the *Journal of the Iron and Steel Institute* (1913, vol. ii. p. 57), where it was given in generous response to my request for information. Then the question of the porosity of clay and the close packing of the clay is of very great importance, because in some cases we desire to have a clay which shall be a non-conductor of heat; but in other cases we desire to have a clay which will allow heat to pass through freely, as, for instance, in a crucible or retort. Thus we want conditions which are to an extent antagonistic; we want one kind of structure for one purpose and one for another. All clay substances conduct heat at approximately the same rate. It is the porosity which to a great extent regulates the conductivity of the clay. The packing of the particles regulates both the porosity and to an extent the fusibility; because, as Dr. Mellor pointed out, the increase in fineness means increased surface, and therefore increased fusibility. This question of packing becomes of interest also in the important direction of moulding sands for cast-iron and for steel, which is by no means an unimportant section of the refractory industry. It is stated in Dr. Mellor's paper that angular fragments give the closest packing, whilst round fragments give the most open packing. That is not always true. For many practical purposes, as in brickmaking, we do not want round particles, because they do not bind so tightly into the surrounding softer matrix, and so form the same kind of structure as sharp particles. But the best and closest packing that can be obtained is with round spheres of different but carefully selected size. If we have three spheres placed together there is a free space between them,

and by putting a smaller sphere, of exactly the right diameter, into that space the whole is packed in a most complete manner. Therefore, theoretically, the proper way is to have two sizes of round particles, one larger than the other; if the sizes are not suitably proportioned a bad result will follow. The ordinary method of measuring porosity is, of course, well known; that is by weighing, first in air, then in water, and again in water after expelling the enclosed air. For foundry sands an interesting method is adopted in America, namely by making a cake of the sand and drawing air through it, and measuring the rate at which the air passes. A similar method might perhaps be used in connection with fire-clay for measuring porosity. I am pleased the Society has taken up this subject, and that so important a discussion has been conducted in the unfavourable times through which we are passing.

Dr. R. S. Hutton (Sheffield): I should like to make two points. First, I want to make a plea for a very much wider extension of research work at high temperatures carried out in electrically heated furnaces. I feel, from work on this subject some years ago, that there is a very rich harvest in that direction, because it is necessary to test refractory materials at very much higher temperatures than those at which they have to be used. When the Electrometallurgical Laboratory was started in Manchester, we set ourselves the task of specially investigating some of the main problems leading up to this industry of refractory materials. We first of all carried out some experimental work on pure silica, which resulted in nothing of very great value to the refractory industry, but it led, at any rate, to the introduction of a new industry in this country—the manufacture of silica glass developed by Dr. Bottomley. We then commenced some work on magnesia, and I think, from what one has heard since, we perhaps discovered a little more than was then widely known amongst makers of refractory materials, but in the first place, the principal point that we discovered was the ease with which magnesia can be obtained in a highly shrunk condition. I was just looking at some notes yesterday, and I found that the cost of doing that on even a small scale was relatively insignificant, because for about 1.15 kw.h. per kilogram one could shrink completely quite high grade magnesia, and the behaviour and properties of the magnesia are undoubtedly different from the ordinary highly calcined magnesia which is largely used in this country by the makers of refractory articles. We were particularly struck at that time by the fact that this material, not to the same extent, but in a very similar way to silica, stood extremely rapid heating and cooling, and I remember thinking that probably the resistance to sudden change of temperature was not only a question of the physical constants that Dr. Rosenhain mentioned, but was also closely associated, as I think he indicated, with the complete shrinkage of the material. Once you get completely shrunk material like alumina or magnesia—generally, of course, the shrinkage is associated with a change of physical state—you get a material capable of withstanding very sudden heating and cooling. I am very pleased to hear that the National Physical Laboratory is going in for a wide extension of research work at high temperatures particularly, because it will help us so much at the limit of temperature to which all industrial fuel furnaces are worked, and also for the fact that it will lead to many new and useful discoveries. The other point I wanted to mention, I hope you, Sir Robert, will appreciate as President. In the first volume of our *Transactions* this Society showed great interest in this question of refractory materials. We had a Paper by Mr. E. K. Scott on magnesia which led to a very interesting discussion, covering pretty widely the field of all refractory materials for furnace apparatus, whilst Mr. Beard and myself

published a Paper on heat conductivity of furnace materials, and I think that Paper, which was very widely published at the time, might perhaps have yielded a great deal more from the manufacturers of refractory materials than it did, because, apart from the question of strength and refractoriness, it is extremely important to bear in mind the widely different purposes for which refractory materials are used. Frequently we use almost the same material for a furnace wall that we use to box in the heat as for a crucible or other container through which we wish to drive the heat. In the one case you want the greatest conductivity, and in the other case the least conductivity compatible with other characteristics. I have been particularly interested to see how promising is the application of zirconia in this line. Dr. Harker, I think, was one of the first, at any rate in this country, to suggest using zirconia, perhaps about ten years ago. It was used with an ingenious furnace, made of the material used in the Nernst lamp. I think we ought to remember to give him credit for the work he did at that time. It is surprising how many of these things remain hidden for many years before they are forced by stress of war circumstances or other reasons to be taken up again more actively.

Dr. W. H. Hatfield (Sheffield) : I should like to congratulate the Society on this excellent and instructive evening. I am sure it will prove to be of inestimable value both to the refractory and metallurgical industries. One aspect has been brought home to me very thoroughly this evening, and that is that the scientific side of refractories must belong to a special set of scientific men devoting their whole attention to the subject. In the past, and indeed to-day, it is too frequently in the different steelworks expected, for instance, that if silica bricks in open-hearth furnaces fail prematurely, the chemical laboratory will, by simple analysis, be able to give the management a satisfactory explanation. My experience as the result of a number of such cases is that the analysis is of relatively little assistance. With regard to silica bricks, it is necessary not only that they should stand up to the temperatures, but that they shall resist the slagging action of oxides and incidentally resist erosion, and I can definitely say, and know there are many here who will support my statement, that there is considerable room for improvement in silica bricks as at present manufactured. I venture to say that the disparity in the behaviour of different makes and, indeed, of different consignments from the same makers of silica bricks will run to 100-200 per cent. That variation in efficiency is far too great, and from observations which I have been able to make from time to time on the excellent behaviour of isolated consignments, I am quite sure that attention to the scientific side of the production will be amply repaid. I was much interested in Mr. Johns' remarks, and I can only express admiration for the manner in which he dealt with his side of the subject. I would like to say, in connection with his remarks, that I also have endeavoured to determine the temperature of the acid Siemens steel melting furnaces, taking the temperatures, for instance, during the last half-hour of a dead-mild heat. I eventually gave the matter up as being hopeless to attempt anything like an accurate determination with the means at our disposal.

By the use of optical pyrometers I may say that I came to the conclusion that the apparent temperature inside the Siemens furnace chamber (not the metal itself) was 1,650-1,700°C. I do not think this is far wrong, and I will give my reasons. It seems now to be fairly well established that the melting-point of pure iron is in the neighbourhood of 1,506°C. Now, you may tap an acid Siemens furnace heat containing carbon as low as 0.1 per cent. with sufficient superheat to effectively run large charges into small ingots. That

being so, we must have probably 100° of superheat over and above the actual freezing-point of the steel. When we add to this the fact that the furnace combustion chamber was still pumping in heat when the charge was finished, and allowing for a definite gradient from the heat applied to the heat attained in the steel, the temperature of $1,650-1,700^{\circ}\text{C}$ which I have just given does not seem to be far out. I shall be extremely interested to hear the experience of other investigators in endeavouring to fix a temperature for steel-making furnaces. Indeed, I think that one of the subjects that will have to be tackled most seriously before real progress can be made in dealing with the refractories for the higher temperatures will be the evolution of a suitable and accurate instrument capable of definite calibration for the highest temperatures. It will readily be admitted at the present time that this question of calibration in the range of temperature from $1,300-2,000^{\circ}\text{C}$. is a real difficulty.

I enjoyed Professor Fearnside's lecture, and I would like to congratulate him, particularly upon his common-sense point of view as to the means of progress in the application of science to the refractory industry. It was really pleasing to hear his appreciation of the good foremen. After all, I suggest that a really good foreman may, indeed, be considered as a scientific man in the sense that he is an accurate observer of facts, and that, further, he evidently has the capacity for intelligently correlating series of such correctly determined operations; and therefore it seems to me quite clear that if every scientific man who is in future going into this refractory industry will use the same broad-mindedness that Professor Fearnside expressed to-night, he will, by availing himself of the sound knowledge already in the possession of those connected with the industry, be able to more readily build up the applied science of the subject.

I was much interested in the steel ladle nozzle which our President has placed on the table. If by using magnesite nozzles such an effect could be relied upon it would be extremely useful. I should like to ask him whether he has found magnesite invariably successful for this purpose, or whether magnesite, like other refractories, has occasional lapses. If there is a variation, Sir Robert may be willing to place before us any experience which he has in that direction.

As representing Messrs. John Brown & Co. and Messrs. Thos. Firth & Sons, I should like to say that I know my firms will look with pleasure upon any move made by the Advisory Council for Scientific and Industrial Research to effectively support research work with regard to refractory material. There is obviously, as we have seen to-night, a mass of work which requires doing, and as a result of which both the producers and consumers of refractories cannot help but profit greatly.

Professor F. G. Donnan, F.R.S.: I have not very much to say, except to mention that I received a letter several days ago from Professor Le Chatelier. Perhaps some gentleman can give Professor Le Chatelier the information he wants. He desires to know whether there is any published information in English of a standard quantitative specification for silica bricks suitable for steel furnaces, dealing with porosity, absolute density, apparent density, resistance to crushing, variation of dimensions on heating, and so on. Many speakers to-night have referred to the work of the gas engineers and their standard specification for bricks, and I was very much interested to hear of the silica brick which has been mentioned, and if there is any information which I can send to Professor Le Chatelier I shall be glad to have it.

The **President** : Perhaps I ought to apologize to two gentlemen who have been to a great deal of trouble in preparing Papers, but who have not yet had an opportunity of putting them before us. I refer to Dr. Boswell and Mr. Griffiths. I will ask Dr. Boswell to say a few words on "Refractory Sands."

THE PROPERTIES AND RESOURCES OF REFRACTORY SANDS IN THIS COUNTRY.

Dr. P. G. H. Boswell (Imperial College of Science and Technology) then read the following Paper entitled "The Properties and Resources of Refractory Sands in this Country."

In response to the invitation of the Faraday Society to speak on refractory materials, I cannot do better than give a general account, from the geologist's point of view, of the state of our knowledge of the properties and resources of refractory sands in this country. First, all refractory "sands" are not pure sands; they include a number of related unconsolidated deposits which are frequently sands with a certain amount of clay admixture. The pressing question before the country is whether we can replace the sands hitherto imported from abroad in pre-war times by supplies from our own country. Where we know the properties of those foreign sands accurately, we can certainly do so, and it may be definitely stated that we are able to replace all such foreign sands which we imported before 1914 by material from our own country. But then the economic factor enters, because the margin of profit on sands is so small. That has been pointed out previously. It was cheaper in the case of high silica sands to obtain the Belgian sand which came to our shores as ballast, and even to move it about the country, than to get our own resources of sands and such-like materials from the place at which they were worked into the industrial areas. These questions are under the consideration of the powers that be. I do not think I am giving away any secrets in saying that the Ministry of Munitions, a branch of which I happen to be advising, is desirous of making us self-supporting in such matters as far as possible. At any rate, if we cannot be self-supporting as a country, we should be as an Empire. The work of the Geological Survey has been outlined, and it is a very splendid and complete work. It organizes the collection of refractory materials of all sorts, and the analysis of as many samples as possible, but there is need for much more work than that. As already outlined by other speakers, synthetic research work cannot be done at present by the Geological Survey because of the lack of staff and equipment, however willing the former may be. The research scientists and experimental workers are then required, and that is why, I take it, that in spite of the fact that, as one gentleman remarked, the steelworks solved all their difficulties with regard to sand a very short time after the war broke out, we still have them saying that their materials are not suitable, and asking where they can go for fresh and better supplies! The purely scientific investigation of these

materials must come first then, but it can only go a certain distance. The ultimate tests of these materials must be in the works themselves. Nobody recognizes that better than research workers, and in scientific investigation we shall get far better results by greater co-ordination of effort. When I look at the mass of material that has been written about refractory sands, the English, French, German, and American literature, and the little there is good in it, I realize how necessary it is that one distinct line should be taken up at a time by each investigator and a large number of results carefully collected. If we correlate those results, we shall at any rate be able to eliminate a certain number of materials which it would be no use to try in the works, and so experimental work there need only be concerned with the promising refractory sands and such-like materials.

Refractory sands in this country may be divided into three classes. We have first the high silica sands, in which there is 99 per cent., sometimes 99.5 per cent., of silica, with little alumina and little iron. Then there are the high alumina- and silica-bearing sands, containing 70 per cent. to 80 per cent. of silica, and anything up to 18 per cent. of alumina, with a very small amount of the alkalis and alkaline earths. Finally, we have the group of refractory sands which are not really sands at all. These are known as moulding sands for greensand work. Of these materials a large quantity in the first class was previously imported from abroad, but there was no justification, except the economic one, for that action. We have abundant supplies in this country of high silica sands, and to no small extent they are very freely available. If I may be allowed to refer to a matter a little outside the obvious scope of this discussion, I should like to mention that there is shortly to be published by the Imperial College of Science and Technology, on the instruction of the Minister of Munitions, a memoir upon British resources of high silica sands suitable for glass-making.* Incidentally, the information there given will be of extreme value to all persons interested in high silica (and also alumina-bearing) sands. In that memoir the British resources of sands are detailed, with full descriptions and analyses, chemical, mineralogical, and mechanical. Information is given as to grain-size, and mineralogical descriptions are included of a large number of materials. The Ministry has helped this work forward particularly on account of glass manufacture, and is thus making a real and successful effort to link-up the purely scientific investigators with the manufacturers and users of the materials. That memoir deals with high silica and alumina sands low in iron-content, but at the same time it must be remembered that there are a very large number of sands in this country the iron content of which is too great for them to be included in the memoir on glass-sands, but which will be of very great value as materials for the making of silica bricks, for hearths for the Siemens furnace, etc. With regard to the third class, there has not been any difficulty about the sands for casting iron, brass, bronze, etc., but when we come to the sediments which were imported from abroad for the casting of certain steels, we find that serious difficulty is encountered in getting supplies which will give the same results as were obtained by the use of foreign supplies. The reason is, we did not know the exact properties of those that were used before. Therefore we cannot tell exactly what would be the best British substitute for those materials. In that direction work is going on, and already we are able to report the finding of very similar deposits, though not precisely similar in all respects. At least two geological horizons in this country should be thoroughly searched in this connection: they are the Pliocene and the Lower Cretaceous. The Ter-

* Since published, December 1916: Messrs. Longmans, Green & Co., 1s. 6d. net.

tiary and Cretaceous deposits of the south-west of England are particularly deserving of attention.

The lines of work on these sands may be divided into work on the mechanical analysis, i.e. size of grain and proportion of each "grade," mineral analysis, and also chemical analysis—not so much bulk chemical analysis as analysis of the different grades which are extremely important for moulding purposes. Certain grades are practically missing. Investigation into the water-holding capacity of each grade at intervals of about 10° C., and other lines of work on the porosity, permeability, and conductivity of British and foreign materials, are required. If we can get such work organized by each scientific investigator working in one direction, and at the same time if we can get to know what the works also want, we shall be able to move forward very quickly.

In brief, research on British and foreign refractory sands is desirable in the following directions (among others):—

(i) Mechanical analyses, carried out scientifically, to gain more accurate ideas of grading.

(ii) Chemical analyses of each grade, not bulk analyses only.

(iii) Mineral analyses, to realize the importance of constituent minerals, especially those prone to decomposition which yield the "bonds" of these sands.

(iv) The water-holding capacity at 10° intervals at temperatures below 110° and at suitable but greater intervals above.

(v) The conductivity.

(vi) The refractoriness of each grade.

(vii) Pore space and permeability.

It is to be hoped that before long a detailed account of British resources of refractory sands, with analyses and notes on their peculiar properties, may be in the hands of manufacturers and others. The memoir referred to above on British resources of sands suitable for glass-making contains notes on and analyses of certain crushed rocks and highly silicious materials suitable for refractory purposes. These glass-sands fall under the first two of the classes mentioned above, but the resources suitable for refractory purposes are far larger than those for glass-making.

I finish with the plea that we should have some means of bringing together the variety of interests which are represented at this meeting. I take it we have four distinct bodies to consider: First, the people who are actually using definite refractory materials; then the people who are taking the raw materials and making them up into refractory articles; we have the officers of the Geological Survey and similar workers who are carefully collecting information and carrying out analyses; and finally we have the research workers, who are doing synthetic and experimental work. The number of people working on refractories in this country is really astonishingly large, and there seems to be little or no means of linking them up in any way and seeing how far they are crossing one another's paths. It would be of very great advantage to the country if one of the results of this meeting was to ensure that those interested should know what is actually being done in this country and what is required, in order that a great deal of overlapping and waste of time might be saved.

DISCUSSION.

The General Discussion was resumed by—

Mr. E. Kilburn Scott: Dr. Hutton referred to my work which initiated a discussion in the first session of the Faraday Society, and in which I referred to the electrical production of fused magnesite. I was able to make large quantities, and its use was suggested as a surface coating on bricks for extra high temperature furnaces. Owing to taking up an appointment abroad I did not follow up the work, but I have recently been working on arc flames in connection with fixation of atmospheric nitrogen, and with further experience think it might be possible to electrically fuse the actual bricks. As Dr. Hutton said, the cost of electrically fusing magnesite is not great, and in this connection I would like to enter a protest against the usual talk about cheap Niagara power. We can develop cheap power in this country, for we have the gas, which costs less than water, and which is easier and cheaper and quicker harnessed than water. For goodness' sake stop talking about Niagara power and other water power abroad, for we have materials and cheap enough power here to make most electrochemical and metallurgical products. Chemists and metallurgists would naturally object to electrical experts talking pessimistically at public meetings that such and such chemical products could not be made here. It is time, therefore, that the usual cheap talk about electric power was stopped. Such questions should be left entirely to electrical engineers, who by long training have acquired the knowledge and intuition enabling them to carry out such work successfully and *know what is ahead*.

The manufacture of refractories for electric furnaces is of greater importance than some of the subjects talked about this evening, because electrical furnaces are coming into use very fast, and in some cases the refractories have not only to withstand high temperatures but also have to act as insulators as well. The problems seem therefore more worthy of scientific investigation and discussion than arguments about firebricks, etc., that our grandparents knew sufficient about to make thoroughly well.

In the references to deposits of refractory materials within the Empire mention might well be made of deposits of nodular magnesite at Fifield in New South Wales. This has been used in steel and other furnaces for about eight years.

Mr. W. C. Hancock: This meeting has demonstrated a fact at which many of us have been hammering for many years, and that is that the chemical composition of a refractory material by itself is fallacious, and we are thrown back on a further study of the physical properties of materials. With regard to these, Dr. Mellor has raised the question of texture, or grain-size. That is easy enough to determine in the case of unfired material, and Dr. Mellor referred to some elutriation experiments which have been made, and Dr. Lessing also exhibited in those tubes the results of experiments which he made some time ago in separating the coarser material and the grog from various retort mixtures. I may say that I know of instances, and Dr. Rosenhain will support me, in which a similar method, practically an elutriation process, was tried in works, but the results were not published. But it is not the question of the size of grain of the unfired material, however, that is so important from a practical point of view. We want to investigate the grain of the fired stuff. Dr. Mellor has exhibited a sample of a fired brick

the surface of which has been ground smooth and polished. That is certainly a very useful method, and it is one which I know Dr. Rosenhain employed some ten or fourteen years ago when he very kindly showed me his results. There is, however, a method which would allow of its considerable extension, and that is, by the application of certain of the organic dyes you get a differential staining, somewhat similar to the etching of polished metal surfaces. If we can proceed on the lines of the excellent work of Professor Fearnside on the micrographic study of these materials, with the object of getting at the internal structure of refractories, upon which the life of the material and its most important qualities depend, it would be all to the good. The questions of conductivity, resistance to chemical action, and abrasion are nearly always dependent on physical texture. Some reference has been made during the evening to the question of the study of refractory materials in coke ovens. Owing to the kindness of the Iron and Steel Institute and the management of the Carnegie Trust a sum of money has been allotted for the investigation of that important class of material, and the work has been placed in my hands under the direction of Professor Bone at the Imperial College of Science. I may perhaps be allowed to say that I have endeavoured as far as possible not to start purely scientific investigations on many theoretical points, but I have made it my duty to get into close touch with the builders of coke-oven plant, and here I should like publicly to express my indebtedness for the great kindness I have received at their hands. I have also had an opportunity of consulting many of the brick manufacturers in the country, and I believe that it is only by keeping closely in touch with brick manufacturers and users that the scientific work which has to be done can lead to any really useful results, and I trust that the investigation that we are now carrying out will lead to something which will be useful. It was said in pre-war times that we were depending on foreign sources for the supply of satisfactory materials. That I find, on investigation, is not perhaps so true as it was thought to be. There are a great many materials available here, and we have still a good deal to do, and I am convinced that there are many manufacturers here to-night who are only too willing to make the fullest use of any scientific work that can be done in order to forward the whole position of this country with regard to refractory materials.

THE THERMAL CONDUCTIVITY OF MATERIALS EMPLOYED IN FURNACE CONSTRUCTION.

Here the President called on **Mr. Ezer Griffiths, M.Sc.**, of the National Physical Laboratory, to read his Paper on "The Thermal Conductivity of Materials used in Furnace Construction."

In the design of furnaces for the attainment of high temperature the question of thermal insulation is one of prime importance, both from the point of view of cost of operation and of the life of the furnace. One generally finds that the maximum attainable temperature is limited to an appreciable extent by the leakage of heat through the walls, and often it is possible to effect considerable improvement with but little trouble. For example, in the Laboratory there is a gas muffle heated by a Méker burner supplied with compressed air. The muffle is designed for temperatures of $1,300^{\circ}\text{C.}$ to $1,400^{\circ}\text{C.}$, and to reach this temperature with the muffle in its original form required about four hours' heating. By covering the exterior surfaces with a 2-in. layer of magnesia-asbestos composition the period was reduced to less than two hours, with a considerable increase in the comfort of those working in the vicinity of the furnace. This is not an isolated case, although it may not always be possible to apply the remedy in such a simple fashion.

In this Paper it is proposed to deal with some of the experimental work already accomplished on the thermal conductivity of furnace materials and to discuss the methods of experiment and their results.

Materials employed in the construction of furnaces may be divided into two classes:—

(1) Those used for withstanding the highest temperature and chosen from considerations of refractoriness, mechanical strength, ability to withstand fluctuations of temperature, and chemical action on the furnace charge.

(2) Those employed as backing to the refractory lining so as to conserve the heat as much as possible. In this class low thermal conductivity, together with ability to withstand moderately high temperatures, are the essential features.

Methods of Determining Thermal Conductivity.—It is always desirable to test materials under conditions approximating to those of actual use, and this is especially true of thermal-conductivity work.

The thermal conductivity of non-metallic substances varies greatly with the temperature, consequently a comparison of the conductivities of two materials at one temperature affords little information concerning their relative values at another temperature. It is also an advantage to have the apparatus designed to take specimens of the size in which they are manufactured. This ensures that the data obtained are representative for that class of material.

In the review of the work accomplished by other observers the writer has

endeavoured to indicate the possible sources of error in their methods, so that an estimate may be formed of the reliability of the results.

Review of Investigations on Thermal Conductivity of Refractory Materials.—The data available concerning the thermal conductivity of materials suitable for furnace construction are very scanty, particularly as regards high temperature. This is to be explained largely by the difficulties of the experiments and the fact that the results lack theoretical interest. Of their importance to the industries there can be no question, and it is to be regretted that there is so little information available concerning British productions in comparison with those of foreign countries.

Wologdine (1) working under the auspices of the Société d'Encouragement pour l'Industrie Nationale, made an extended investigation of the thermal conductivity, porosity and permeability to gases of a large series of refractory materials of French manufacture, studying at the same time

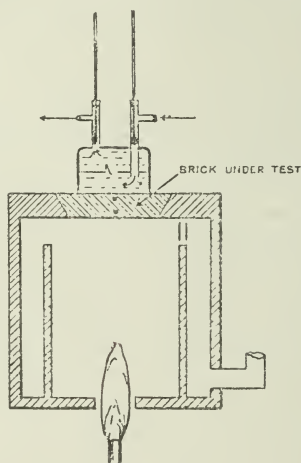


FIG. 1.—Wologdine's apparatus.

the relation of these physical properties to the firing temperature and chemical composition. A diagram of the apparatus he employed is shown in Fig. 1.

The specimen under test was specially made in the form of a circular disc, 5 cm. in thickness, with a bevelled edge forming a portion of the walls of a gas-heated muffle. The temperature gradient through the slab was obtained by embedding two platinum-platinum rhodium couples at a depth of 5 mm. from each face. An additional thermoelement in the air near the hot face gave the furnace temperature.

The heat transmitted through the slab was measured by a flow calorimeter in the form shown in Fig. 1.

The design of the calorimeter is the weakest point in the method, since the presence of a cooled area on the upper surface must distort the flow lines from normal. A guard ring around the calorimeter would have eliminated this source of error.

The couples were calibrated by reference to the freezing-points of copper, common salt, and aluminium, together with the boiling-points of sulphur and naphthalene. With the exception of sulphur the values assumed for these fixed points are in fair agreement with the values accepted at the

present time. For the boiling-point of sulphur the value 455° was taken instead of the generally accepted value 444.5° .

In the case of each material samples were fired at two temperatures, $1,050^{\circ}\text{C.}$ and $1,300^{\circ}\text{C.}$, so that the influence of the firing temperature could be ascertained. Unfortunately these temperatures, in the case of many of the materials, do not correspond to those employed in modern manufacturing practice.* Consequently the data obtained by Wologdine cannot always be accepted as applying to commercial varieties of bricks of the same composition.

Three conclusions of general interest can, however, be deduced from Wologdine's work :—

1. That the conductivity increases with the firing temperature. For example, silica bricks burnt at $1,300^{\circ}\text{C.}$ have a conductivity 50 per cent. greater than those burnt at $1,050^{\circ}\text{C.}$
2. That there is an increase in thermal conductivity with temperature for all materials, with, perhaps, the exception of chromite brick, in which case the conductivity is nearly constant.
3. That the conductivities of carborundum ($\text{SiC} = 87$ per cent., $\text{SiO}_2 = 12$ per cent.), and graphite ($\text{C} = 48$ per cent., $\text{SiO}_2 = 30$ per cent.) bricks are of the order of 4 to 6 times those of fire-clay bricks.

In Table II some of Wologdine's numerical results are compared with those obtained by other observers employing materials of approximately the same chemical composition.

A comprehensive investigation of the properties of British refractories on the same general lines as that of Wologdine's would undoubtedly lead to conclusions of value, particularly if, in addition, the following properties of the materials were studied :—

1. Crushing strength at high temperature.
2. Permanent expansion or contraction on heating and coefficient of thermal expansion.
3. Ability to withstand rapid fluctuations of temperature.
4. Influence of the density of the material.

Dougill, Hodsman, and Cobb (3) investigated the thermal conductivities of some fire-clay, silica, and magnesia bricks. Their apparatus was somewhat similar to Wologdine's, but designed to take ordinary sized samples. The heat transmitted was measured by the evaporation of water from a vessel cemented on to the top surface of the brick. This calorimeter was composed of a large vessel 9 in. long by $4\frac{1}{2}$ in. wide by 3 in. high with a plane base. Within the larger vessel was fixed the calorimeter proper, consisting of a chamber 4 in. long by 2 in. wide by $2\frac{1}{2}$ in. high. Steam distilling from this inner vessel passed through a sloping tube to the condenser, the water being collected in a measuring jar. The usual rate of evaporation was about 5 c.c. per minute. The authors state that it was found advantageous to surround the inner chamber with a non-conducting jacket, and for this purpose sheef rubber was found to be satisfactory.

In the writer's opinion, it would be better if in this method the calorimeter was entirely separated from metallic connection with the larger vessel, since the existence of a slight gradient of temperature across the metal base would seriously vitiate the results. In fact, a narrow separation gap, as perfect thermally as possible, is the essential feature of the guard-ring idea.

An interesting fact brought out by their investigation is the marked

* Marshall (2) states that the usual firing temperature of silica bricks is 125° to 225° higher than for clay bricks. For the latter he mentions the value $1,500^{\circ}\text{C.}$ and $1,610^{\circ}\text{C.}$ for silica, referring presumably to American practice.

decrease with temperature in the thermal conductivity of magnesia,* as the data in Table I show.

TABLE I.

Temperature.	True Conductivity (calculated from Smoothed Curve through Experimental Observations). C.G.S. Units.
300°	·0187
500	·0140
700	·0107
900	·0089

They found that the conductivity of silica brick did not differ appreciably from that of fire-clay brick, and both were only about one-fifth that of magnesia at 500°.

Wologdine had observed that silica bricks possessed a lower conductivity than fire-clay bricks. The discrepancy may be due to the fact that his samples had been fired at lower temperatures.

Boyd Dudley (4) carried out some experiments on fire-clay, silica, and magnesia bricks of American manufacture. The material under test constituted one wall of a furnace heated by means of by-product coke. By careful regulation of the draught a uniform combustion through a depth of 26 in. was obtained. The bricks composing the wall were 9 in. by $4\frac{1}{2}$ in., and built so as to produce a flat surface. The heat transmitted through a definite area of the wall was measured by a flow calorimeter 8 in. by 8 in. fitted with a guard ring.

A period of eight to nine hours was allowed to elapse after starting the fire before observations were commenced.

The temperature gradient through the bricks was obtained by means of a platinum-platinum rhodium couple inserted to various depths in holes bored to within $\frac{1}{4}$ in. of the inner face; measurements being made every $\frac{1}{4}$ in. to within $\frac{1}{4}$ in. of the cold face.

This method of ascertaining the temperature at various points is simple, but suffers from the disadvantage that the couple wires are perpendicular to the isothermal planes and the readings may be vitiated by conduction along the wires cooling the junction. That this may lead to serious error is shown by some observations of Nusselt (5), when working on the thermal conductivity of materials at low temperature. He observed that two couples† at the same point, one parallel and the other perpendicular to the isothermal surfaces, differed by 40° at a true temperature of 100° C., the one perpendicular to the isothermal surfaces reading low owing to conduction. To obtain the temperature at a point in a poorly conducting material (across which there is a steep gradient) it is necessary to place the thermoelement in the isothermal surface passing through that point for some distance before leading out the wires.

* It might be remarked that the magnesia referred to is not the white flocculent material (basic carbonate) employed for steam-pipe lagging, but a dense fine-grained brick (known in the trade as Mabor) which has been fritted at a high temperature. The material is of great utility in experimental work at high temperatures, since it can be sawn and machined without difficulty.

† In this case the wires were of iron-constantan .6 mm. in diameter. Dudley does not mention the diameter of the thermocouple wires.

TABLE II.

Approximate Analysis.	Temp. Range.	Mean Temp.	Conductivity.	Authority.	Remarks.
<i>Fire-clay Bricks.</i>					
78 % SiO ₂ : 18 % Al ₂ O ₃ 3·3 % Fe ₂ O ₃ : 0·5 % CaO	950° to 135°	542°	·0037	Wologdine	Burnt at 1,050°
Ditto	860° to 260°	560°	·0050	Wologdine	Burnt at 1,300°
66 % SiO ₂ : 29 % Al ₂ O ₃ 4 % Fe ₂ O ₃ : 0·5 % CaO	1,160° to 227°	693°	·0035	Wologdine	Burnt at 1,050°
Ditto	1,000° to 227°	614°	·0042	Wologdine	Burnt at 1,300°
66 % SiO ₂ : 31 % Al ₂ O ₃ 1 % Fe ₂ O ₃ : 1 % Alk	— 600° 1,000°	·00305* ·00405	}	Dougill, Hodsman, and Cobb	Hard-fired Seger cone, 10-11 (about 1,330° C.)
53 % SiO ₂ : 43 % Al ₂ O ₃ 2 % Fe ₂ O ₃ : 1·5 % Alk	— 100° 1,000°	·00169* ·00339			
<i>Silica Brick.</i>					
94 % SiO ₂ : 1 % Al ₂ O ₃ 2 % Fe ₂ O ₃ : 2 % CaO	1,000° to 110°	555°	·0020	Wologdine	Burnt at 1,050°
Ditto	930° to 150°	540°	·0031	Wologdine	Burnt at 1,300°
95 % SiO ₂ : 2 % Al ₂ O ₃ 1·1 % Fe ₂ O ₃ : 1·5 % CaO	1,200° to 390°	785°	·0036	Dougill, Hodsman, and Cobb	Coarse grained
96 % SiO ₂ : 0·9 % Al ₂ O ₃ 0·8 % Fe ₂ O ₃ : 1·8 % CaO	— 100° 1,000°	·0022* ·00425	}	Boyd Dudley	
<i>Magnesia (or Magnesite) Brick.</i>					
95 % MgO ; 1 % SiO ₂	1,000° to 230°	615°	·0058†	Wologdine	Burnt at 1,050°
Ditto	750° to 175°	462°	·0065†	Wologdine	Burnt at 1,300°
92 % MgO : 5 % SiO ₂ 1·6 % Fe ₂ O ₃ : 1·7 % CaO	560° to 325°	442°	·0151	Dougill, Hodsman, and Cobb	Fine grained
	1,370° to 690°	1,030°	·0091		
86·5 % MgO : 21·5 % SiO ₂ 7·0 % Fe ₂ O ₃ : 2·7 % CaO	830° to 445°	638°	·0135	Boyd Dudley	Made from dead burnt material, Dense and hard

* Calculated from smoothed curve through experimental points.

† This low value may be due to the want of compactness in the brick mentioned by Wologdine.

Dudley found that the conductivity of magnesite was practically constant between 445° and 830° ; while Dougill, Hodsman, and Cobb have shown that the conductivity of their magnesia decreased with temperature, but that the coefficient diminished with increase of temperature, as shown by Table I.

Clement and Egy (6) studied four samples of fire-clay bricks (American). The specimens were in the form of hollow cylinders with two longitudinal holes for the insertion of thermocouples. The heat was supplied by means

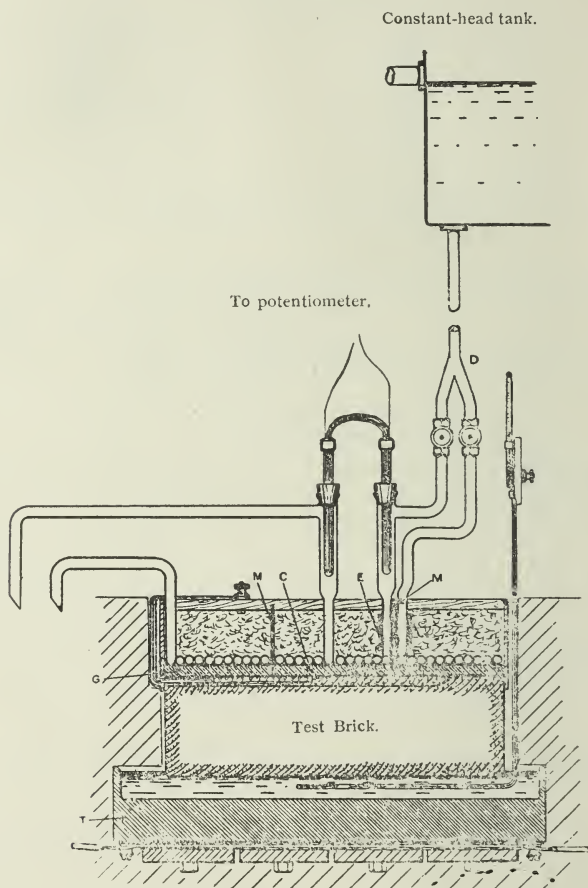


FIG. 2.

of a coil of nickel wire wound on a porcelain tube fixed along the axis of the specimen. In this case the heat supplied per unit length was calculated from the electrical energy dissipated in the coil.

The method is theoretically sound, but has the practical disadvantage of requiring specimens of special form, and there is some uncertainty in the measurement of the radial distances of the points at which the temperatures are measured. No analysis is given of the material or any indication as to its composition beyond the few remarks concerning the structure.

The writer some time ago designed and constructed the apparatus shown in Fig. 2 for tests of specimens in sizes as manufactured for general use.

The work so far has been concerned with the conductivity of materials

whose principal property is low thermal conductivity. One of the practical difficulties to be overcome was the attainment of a uniform temperature over the hot face of the brick, which surface was always irregular and generally exhibited slight curvature in addition. This difficulty was surmounted by transmitting the heat to the brick by means of a molten metal which adapts itself to the irregularities of the surface. For this purpose tin has been employed at low temperatures, and has proved entirely satisfactory except for oxidation with

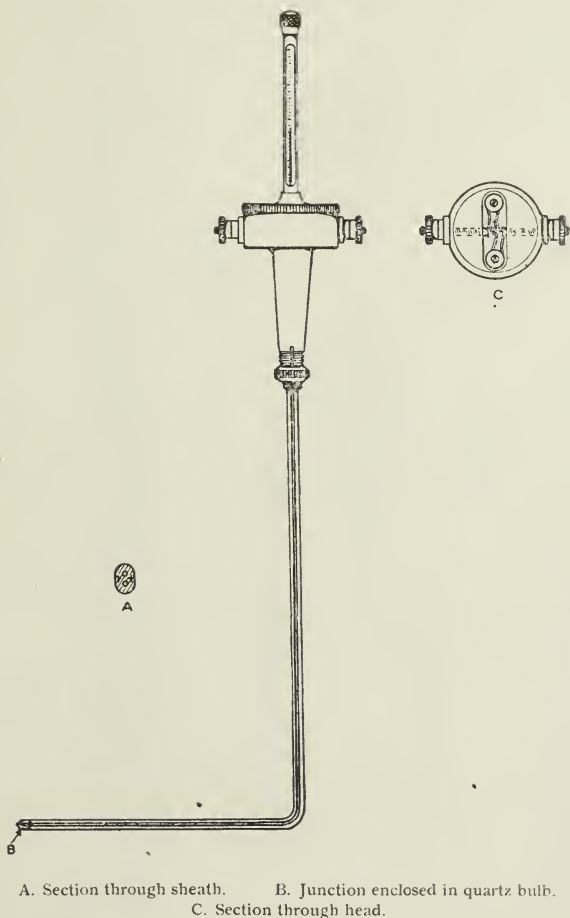


FIG. 3.

time. The cast-iron tray T has a uniformly distributed heating coil attached to its under surface. The depth of the molten metal is about 1 cm., and the brick under test rests on three projections, so that the free surface of the tin around the edges stands at a level of about 2 mm. above the immersed surface of the brick.

The temperature of the molten tin was obtained by means of a platinum-platinum iridium couple. The details of the construction of this couple are shown in Fig. 3.

The wires were separately insulated in the quartz tubes, which are

enclosed in an outer sheath,* the external diameter of which was approximately 5 mm. The bulb B was sealed off in the oxycoal-gas blowpipe after the insertion of the wires, and no difficulty was found in bending the tube into the L form with the wires *in situ*, provided the heating was not unduly prolonged. By rotating the couple the temperature distribution over a wide arc could be explored, and the insulation of the quartz was sufficiently good to prevent any leakage from the heating circuit into the potentiometer.

The temperature of the cold surface of the brick was determined by several iron-eureka (constantan) thermocouples bedded just flush with the surface. The calorimeter was attached to this surface by means of a thin layer of Purimachos cement.

The construction of the flow calorimeter will be understood from Fig. 2. The guard ring G is separated from the calorimeter proper C by a narrow gap about 1 mm. wide, the space being filled with mica plates M set on edge so as to produce a level surface. The inflowing water divides at D, and flows through adjacent turns of piping in the calorimeter and guard ring. Since the temperatures of the two streams are the same, this tends to eliminate any gradient of temperature across the gap separating the calorimeter from the guard ring. The ratio of flow was adjusted to produce equal temperature rise. Differential couples of 6 pairs of copper-constantan measured the rise in temperature in the water flowing through the calorimeter. The tube containing the inflow couple is separated from metallic contact with the calorimeter by a short connecting piece of ebonite E. A steady stream of water is obtained by the constant-level tank shown, and the rate of flow through the calorimeter determined by the time required to collect one litre of water.

In order to detect any systematic errors the experimental conditions were varied by altering the rate of flow, changing the differential couples, and the thickness of slab experimented on.

The results were in agreement within the limits of experimental error, and there is little doubt that the limiting factor in the accuracy is due to the inherent properties of the materials themselves, such as slight variations in homogeneity and thickness.

In experiments at temperatures above 450° the hot face was maintained at a uniform temperature by pressing it against a flat iron plate forming a portion of the wall of a large uniformly heated muffle. In this case the hot-face temperature was determined by bare nickel copper *vs.* nickel chromium couples of No. 19 gauge wire cemented on the surface.

Data for the same sample over the same temperature range obtained by the two different modes of heating were in close agreement; the molten metal bath method giving more concordant results than the muffle method.

One precaution was found to be essential in working with thick samples of materials of low thermal conductivity, namely, to allow ample time for the equilibrium state to be set up at each steady temperature. Inspection of the data in Table III shows that a complete series on a specimen extend over several days.

Of the variety of materials tested with this apparatus, those of interest in connection with furnace construction are the following: diatomaceous brick and slag wool or silicate of cotton mats: the one a solid brick, the other a compressible packing material.

Diatomaceous Bricks.—The principal constituent of these bricks is known by a variety of names, such as diatomite, kieselguhr, infusorial earth, etc. The material is found in large deposits in Ireland and various parts of the world, being widely distributed. After purification the raw material is

* The fused silica tubing was obtained from the Silica Syndicate.

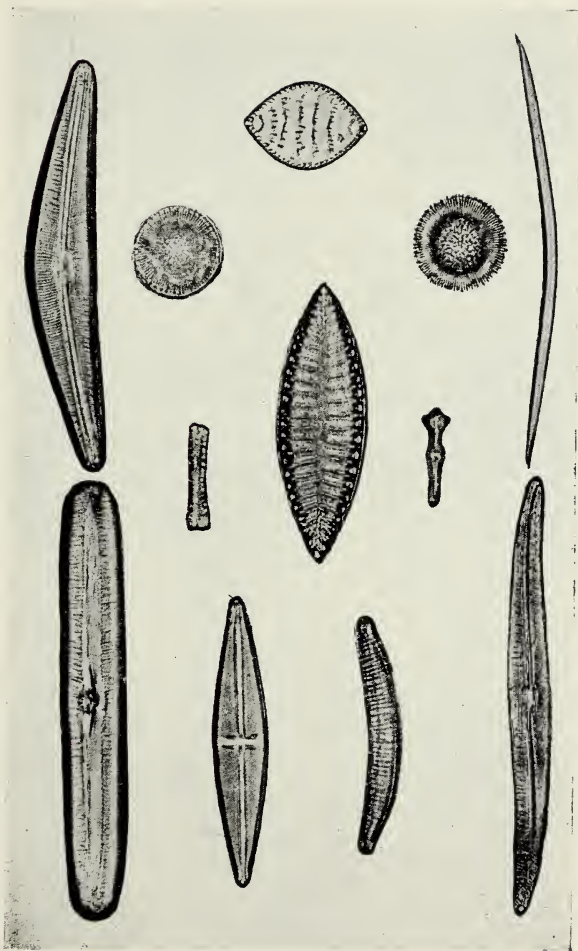


FIG. 4.—Photomicrograph of Diatoms.

almost entirely composed of the silica shells of diatoms. The formation of these shields or skeletons by Nature is not fully understood, but it appears to be due to the reaction of the chlorophyll masses composing the plants with the soluble inorganic salts in water under the influence of sunlight. A photomicrograph of some individual diatoms is shown in Fig. 4. The heat insulation property of the material is due to the minute air cells enclosed by the silica walls.

The raw material after calcination is a light grey powder composed of about 92 per cent. of silica (SiO_2), the remainder being oxides of iron, aluminium, calcium, and of the alkali metals.

For making up into bricks and tiles the powder is mixed with a little clay to act as binder, then moulded, and fired at a temperature in the neighbourhood of 900°C . The final product is a light porous brick of apparent density about 0.64 gm./c.c. It has a fair compressive strength, about 400 lb. per inch, but is friable and will not stand abrasion.

For a fritted brick the material has an extremely low thermal conductivity, and its refractory nature permits of its use to high temperatures if suitably protected from the cutting action of flames and abrasion.

A typical series of observations on the variation with temperature in the thermal conductivity of a tile measuring 8 in. by 12 in. by 2 in. thick are shown graphically in Fig. 5, while the data are summarized in Table III.

TABLE III.

Diatomaceous Brick.

Date. Oct.	Time.	Temp. Hot Face.	Temp. Cold Face.	Mean Temp.	Conductivity* in C.G.S. Units.
25th	10 a.m.	186°	24°	105°	.000310
24th	11 a.m.	261	26	144	.000318
24th	9 p.m.	275	26	150	.000317
23rd	9 p.m.	287	25	156	.000331
22nd	11 a.m.	453	27	240	.000360
22nd	8 p.m.	458	28	243	.000362
22nd	1 a.m.	505	28	267	.000359
21st	8 p.m.	517	28	272	.000371
21st	11 a.m.	598	32	315	.000387
20th	8 p.m.	622	32	327	.000384
26th	10 a.m.	893	62	478	.000447
25th	10 p.m.	939	64	502	.000461

Since the efficiency of the material as an insulator is largely determined by the air spaces enclosed in the minute cells, it is to be expected that samples obtained from different sources would vary in their conductivity according to the amount of purification from silica sand and grinding the material has received.

By deliberately grinding the material finely, it should be possible to completely destroy the structure of the grains, so that the insulating power would be no greater than that of silica sand. Consequently the figures given in Table III refer only to bricks of high-grade material, and the writer has

* To convert conductivities in C.G.S. units to B.T.U.'s per square foot per hour per 1°F . difference per 1 in. thickness multiply by 2,900.

obtained values 25 per cent. greater with some diatomaceous bricks which on mere inspection would appear identical with the above.

Slag Wool.—This is a fibrous material resembling cotton-wool in appear-

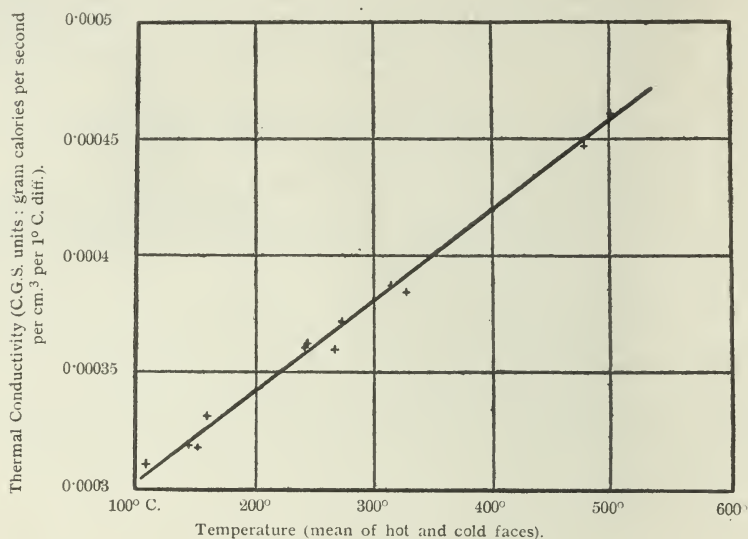


FIG. 5.—Diatomaceous Brick.

ance. It is manufactured by blowing steam through molten blast-furnace slag. Chemically the material is largely composed of calcium aluminium

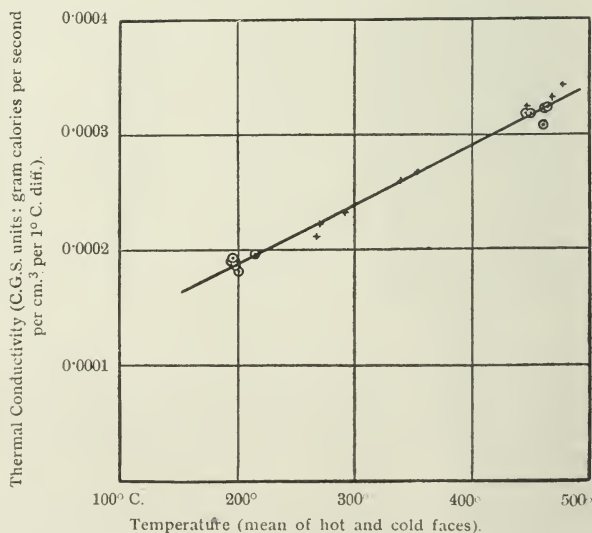


FIG. 6.—Slag Wool Mats.

silicate (CaO 36 per cent., Al_2O_3 23.5 per cent., SiO_2 31 per cent. The material tested was made up in the form of compact mats, with galvanized wire

meshing over each face connected together at intervals by loops of wire threaded through the slag wool.

The apparent density was 0.24 gm. per c.c.

The material is an excellent insulator, as the data below show, and is capable of withstanding a fairly high temperature without losing its fibrous structure. It should not, however, be heated for extended periods to temperatures exceeding about 750° C.

TABLE IV.

Slag Wool.

Temp. Hot Face.	Temp. Cold Face.	Mean Temp.	Conductivity in C.G.S. Units.
482°	51°	266°	'000212
486	52	269	'000222
518	55	292	'000232
615	62	338	'000259
634	71	353	'000266
802	90	446	'000324
842	75	469	'000331
852	100	476	'000342
<i>Another Sample from same Stock.</i>			
324	65	194	'000191
322	69	195	'000194
325	69	197	'000185
324	69	197	'000187
335	65	200	'000181
352	74	213	'000197
700	192	446	'000318
702	195	449	'000318
718	203	460	'000308
723	200	462	'000324
723	204	463	'000323

White Magnesia.—This material is commonly used for steam-pipe covering and similar purposes. It is composed principally of basic carbonate of magnesium with about 15 per cent. of asbestos fibres as binding material. While its thermal conductivity is low (about .00017 C.G.S. units between 20° and 350°), it cannot be employed at high temperatures without undergoing chemical decomposition. At temperatures exceeding about 350° carbon dioxide is given off, and uniform heating to temperatures of the order of 700° reduces the material to a loose powder. In this state it possesses a considerably higher thermal conductivity, and the writer has observed 100 per cent. increases in conductivity of samples so treated.

This, however, does not limit the use of magnesia to low temperatures, since in the majority of cases there is a considerable gradient through the material and only a small layer nearest the hot region reaches the decomposition stage.

For a hot face temperature of 600° C. and cold face 20° the conductivity is about .00022 C.G.S. units.

In conclusion the writer desires to express his thanks to Messrs. Frederick

Jones & Co., Kentish Town, for permission to publish data obtained in tests on their behalf; to the Diatomite Company, Manchester, for the photomicrograph; to the Director of the Laboratory, Dr. Glazebrook, for his encouragement and interest in the work; and to Dr. Harker for many valuable suggestions.

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DISCUSSION.

The **President** : No one has studied the question of high temperatures and furnace work more than Dr. Harker, and I am sure that the meeting would not wish to separate without hearing him.

Dr. J. A. Harker, F.R.S. : At this hour I will really only add a few words. The first remark I want to make is that I think the Paper which was given to you with such admirable brevity by Mr. Griffiths is well worthy of more study than would appear from the brief abstract which he gave. The work described is of a very difficult character, and Mr. Griffiths has begun quite well by telling people how very hard it is to collate from a series of sources such a tremendously involved mass of material as that dealing with the thermal conductivity of refractory materials. There is one thing I want to call attention to, and that is how utterly different measurements of thermal conductivity are from most measurements, in that at first you ought to be content and very pleased if you get the right number of zeros in your result. It does not mean that you know to 5 per cent. or 1 per cent., and that nothing beyond that counts, but you want to know whether you ought to have four zeros or three zeros before you attempt to apply your result, and Mr. Griffiths has by his methods given a very complete justification of the accuracy of both of them by showing that for the same material they both join up and give a straight line. It shows that both methods, quite independently of one another, agree, and that is a great deal to be said for them. That little thermo-couple for exploring round the corner is a very neat dodge

indeed for getting rid of one of the most grave difficulties in getting the right thermal conductivity of such an irregular sample as a slab of refractory material 9 in. square and about 3 in. wide. In that connection there is one other thing—it is one of those questions where the nearer you approach the works conditions the harder does your laboratory work become, because of the enormous time taken to get good results. If I were asked to name a subject in which it was easiest to cook results, I should say there is nothing easier than to cook results of thermal conductivity with such a substance, if you try to imitate a furnace wall with a layer 8 in. thick. The same sort of thing happens with high temperatures as occurs with a refractory material for thermal insulation at low temperature. I think Mr. Griffiths is to be congratulated on a result he has obtained on a very difficult piece of work.

Zirconia has been mentioned, and Dr. Mellor said that if you make a tube like an ordinary potter and take the greatest care in getting the smallest particles you can obtain a material which, though not like a silica material, will stand heating, and can be plunged into water and nothing happens. If it is so, then that is a valuable difference between zirconia and some of the other clays we have been discussing.

Dr. H. C. Greenwood was greatly interested in Mr. E. Griffiths' discussion of the effect of temperature on the thermal conductivity of refractories. He thought that the question of good conductivity, as opposed to good insulation, was worthy of more attention than it often received. In the melting of non-ferrous alloys, for example, the conductivity of the crucible was of considerable importance, both as regards time and fuel consumption, the time for a melt being much greater with a clay crucible than with a plumbago one.

In this connection the properties of carborundum were very interesting and could often be turned to advantage in electric furnace design. The desirability of taking into consideration the conductivity of bricks, etc., used in the construction of externally heated muffles did not appear, however, to be properly appreciated by furnace designers.

Further experiments on the thermal conductivities of materials like magnesia and carborundum at temperatures between 1,000° and 2,000° C. would seem advantageous, although such measurements naturally involve considerable difficulties.

The writer had found, by indirect observations, in the course of an investigation on the boiling-points of metals, that the thermal conductivity of fused magnesia at a temperature of about 2,300° C. seemed to be fairly high.

A series of high temperature conductivity measurements would be of great value in connection with steel-melting crucibles, regenerators, etc.

Mr. C. R. Darling (*communicated*): Reference to the Paper read by Mr. Griffiths shows that the various types of firebrick possess, on the average, a conductivity ten times as great as materials of the type of slag-wool. This fact led to the suggestion by Dr. Hutton and Mr. Beard, in a paper read before the Faraday Society in 1905, that industrial furnaces could be with advantage lagged with a substance of high insulating power. Fitzgerald,* using an experimental furnace, found that the heat escaping was reduced by 50 per cent. when lagged to a thickness of 1 in.; and the present writer has shown † that in the case of an annealing furnace, working at 800° to 900° C., the financial saving effected by such a lagging would amount to nearly

* *Transactions of the American Electrochemical Society*, vol. 21, 1912.

† *Cantor Lectures on Methods of Economizing Heat*, 1913.

2s. per annum for each square foot of exposed surface. For some reason, however, it is not possible to get metallurgists to interest themselves in this matter, although, in addition to saving money, the use of a lagging would greatly reduce the temperature of the surrounding air, and make the conditions more comfortable for the workmen. An unlagged furnace should be as rare as an unlagged steam-pipe. One of the most useful refractory materials, from a laboratory standpoint, is alundum, which melts at $2,050^{\circ}\text{C}$. It is one of the few materials which have no action on platinum at high temperatures, and is therefore well suited for platinum-wound electric furnaces. It can be made into perfectly regular shapes, and in this respect is superior to silica; but on the other hand it is not capable of resisting sudden temperature changes so well as silica. A non-porous variety, impervious to furnace gases, is now procurable, which forms a satisfactory sheath for pyrometers, and is less corroded than silica when immersed in molten metals. In a high-temperature research on which I am at present engaged, and in which the President has kindly interested himself, the question of the electric conductivity of refractories at high temperatures has arisen. Little work has been done on this subject, probably owing to its restricted importance; but as an example Northrup has shown that the resistivity of alundum falls from 6,100 ohms at $1,100^{\circ}\text{C}$. to 190 ohms at $1,600^{\circ}$. In the research referred to a refractory is required which shows no signs of pyro-conduction up to $1,600^{\circ}$, and is not easily attacked by metallic oxides. I should be grateful if any British maker of refractories would furnish me with a material possessing these qualifications.

A CARBON TUBE FURNACE FOR TESTING THE SOFTENING POINTS AND COMPRESSIVE STRENGTHS OF REFRACTORIES.

The following Paper by **Mr. Ezer Griffiths** and **Mr. Edgar C. Griffiths** on "A Carbon Tube Furnace for Testing the Softening Points and Compressive Strengths of Refractories" was read and discussed before the Society on Monday, December 18th, 1916.

The search in recent years for refractory materials suitable for high temperature work in the laboratory and in industrial practice has led to the discovery of many interesting substances possessing peculiar characteristics. A knowledge of the physical properties of such materials at high temperatures is necessary to determine the appropriate treatment during manufacture and in subsequent use. The life of the refractory lining of a furnace is dependent on a variety of factors: the softening temperature, compressive strength, thermal conductivity, thermal expansion, permanent expansion or contraction, and ability to withstand sudden temperature changes; the relative importance of these depends on the construction of the individual furnace. Hence it is preferable to study the various physical properties individually rather than attempt to imitate industrial conditions on a laboratory scale.

The softening point and compressive strength under load are the two fundamental properties of a refractory, and to effect measurements of these at high temperatures the furnace described below was constructed. Temperatures exceeding $1,800^{\circ}\text{C}$. had to be arranged for, consequently a carbon tube type of furnace was adopted.

A general view of the external appearance of the furnace is shown in Fig. 1, while a section is given in Fig. 2. The carbon tube C is 2 in. outside diameter, $1\frac{1}{2}$ in. inside diameter, and 11 in. long. Except over the portions covered by the electrodes a slot $\frac{1}{4}$ in. wide extends the entire length of the tube, the object of which is to permit of temperature observations on the specimen heated in the furnace. A slot was made in preference to a round hole, since the latter would have produced a discontinuity in the resistance of the tube.

To increase the resistance the tube was ground down slightly over the greater portion of its length.

The sheet-iron casing A is 12 in. in diameter, and the ends are closed with two pieces of asbestos slate board B B. This material is cheap and fireproof.

Crude zirconia* powder is used as thermal insulation† around the tube, and outside this a 3-in. layer of magnesia asbestos lagging. Zirconia in a finely divided state is a very good insulator, and will stand high temperatures without fusing; it begins to frit at about $1,100^{\circ}\text{C}$. In contact with hot

* The crude mineral is known as baddeleyite (ZrO_2 75 per cent., SiO_2 13 per cent., Fe_2O_3 3.5 per cent., TiO_2 3.5 per cent.) ; density about 4 grams per c.c.

† A layer of electrically shrunk magnesia was inserted between the zirconia and the carbon, since magnesia does not react with carbon and is very refractory melting-point, $2,800^{\circ}\text{C}$.).

carbon, however, it readily forms a carbide, and this sinters to form a solid tube around the carbon.

Method of applying the Pressure.—The pressure on the test specimen is applied by means of the plunger arrangement shown. The two springs of practically identical strength are attached one at each end to the crossbar D over the central plunger. The other ends were fixed to collar E, which could be screwed up and down the fixed tube F by means of the handwheel G. Rotation of the springs with the handwheel is prevented by the keyway in the tube F. The magnitude of the pressure could be read off the graduated scale H. The pressure device is carried on the arm K, which can be swung around one of the vertical pillars to give free access to the top of the furnace.

With the springs shown pressures up to 150 lb. per square inch can be applied.

The sample to be tested is in the form of a short cylindrical rod, the usual size being $\frac{3}{8}$ in. diameter and 1 in. long. If the material is in the form of a brick a piece is chipped off and ground to the desired shape. The specimen is supported in the furnace on a carbon rod, while a similar rod on top transmits the pressure.

The scale H was calibrated by observing the readings corresponding to definite tensions applied to D by means of a spring balance.

The various parts were machined from aluminium alloy (Al 77 : Zn 20 : Cu 3).

Construction of the Electrodes.—A constructional detail of vital importance in connection with carbon furnaces is the electrodes. Currents from 100 to 1,000 amperes have to be transmitted across a metal carbon contact, and any appreciable resistance at this junction will result in troublesome heating effects and finally in arcing. Even if by careful construction the contact resistance is reduced to an insignificant value the heat conducted along the hot resistor is still an important factor. Hence provision must always be made for cooling the electrodes.

In the early experiments of Lummer and Pringsheim heavy copper plates were used to conduct the heat away and dissipate it by radiation and convection, but in practically all modern furnaces water cooling is resorted to since this has been found to be both simple and reliable. For furnaces of laboratory scale quite a small stream of water suffices (of the order of 2 to 3 c.c. per second), provided the electrodes are carefully fitted. The earliest types of water-cooled electrodes are those of Hutton. They consisted of hollow massive boxes of brass through which water circulated.

The bore of the electrodes was accurately turned to fit the carbon tube, which was copper-plated and soldered into position. This form of electrode construction is entirely satisfactory, but is somewhat troublesome to construct owing to the necessity of brazing together the joints of the box and the special treatment of the carbon tube.

The details of the construction of the electrodes of the present furnace will be understood from Fig. 3. A copper tube was bent into a zigzag form for each half-electrode. Fusible metal (white bearing metal) was then cast around the tube, the mould being formed of strip iron with the carbon tube as core. By this means a casting was obtained whose bearing surfaces must necessarily be an exact fit on the carbon tube, and there is no necessity for machining the metal faces or grinding the end of the tube. With a current of about 400 amperes through the tube the drop potential across the contact was less than $\frac{1}{10}$ volt, the smallest quantity detectable with the A.C. instrument available.

When the same electrodes are used for tubes differing slightly in

diameter it is advisable to insert a few sheets of tinfoil to distribute the pressure evenly over the surfaces, since in practice it is impossible to obtain two tubes of exactly the same diameter or absolutely circular in cross-section. The variations do not appear to be due so much to dies through which the tubes are extruded as to subsequent shrinkage and deformation during the firing process.

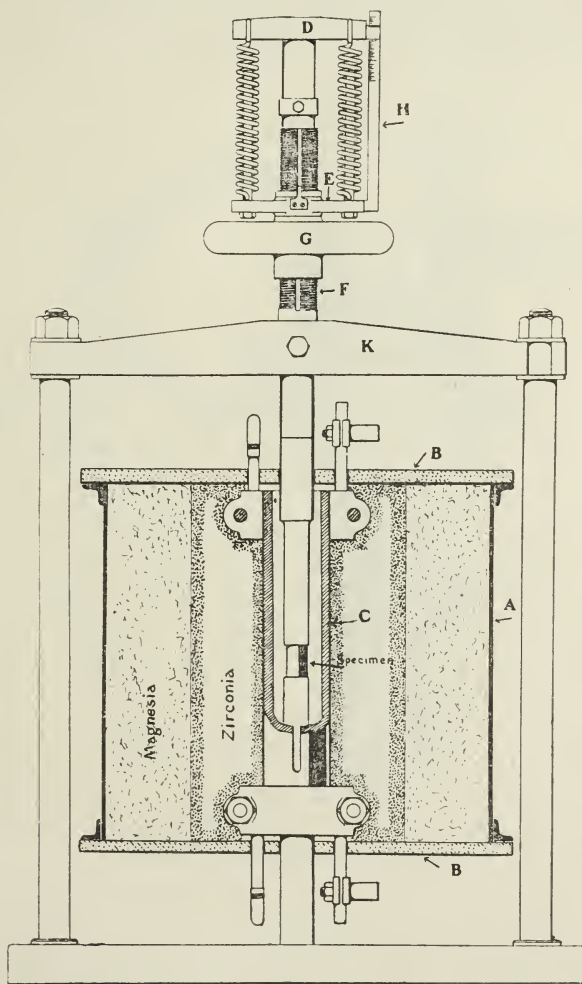


FIG. 2.

In passing, we may mention another simple type of electrode construction which has been found satisfactory in the past. This is shown in Fig. 4. It was designed for a large $5\frac{1}{2}$ -in. crucible furnace. The two blocks of graphite, L L', are bored to the external diameter of the tube. The current is supplied by the water-cooled copper tube M soldered to the flat copper strip N. Current is also supplied to the block L' by the flexible copper conductor O, so that the current density across the contact surfaces is quite low.

A point which must always be attended to in furnace construction is to make provision for the expansion and contraction of the tube on heating and cooling. Changes of length amounting to several millimetres take place, and the tube must either be able to slide through the electrode or preferably one of the electrodes must have sufficient flexibility to move with the end of the tube.

If the connections are too rigid it is generally found that the tube breaks on cooling after exposure to high temperature. The same difficulty does not arise in the case of the graphite spiral furnaces, since there the spiral forms allows ample flexibility.

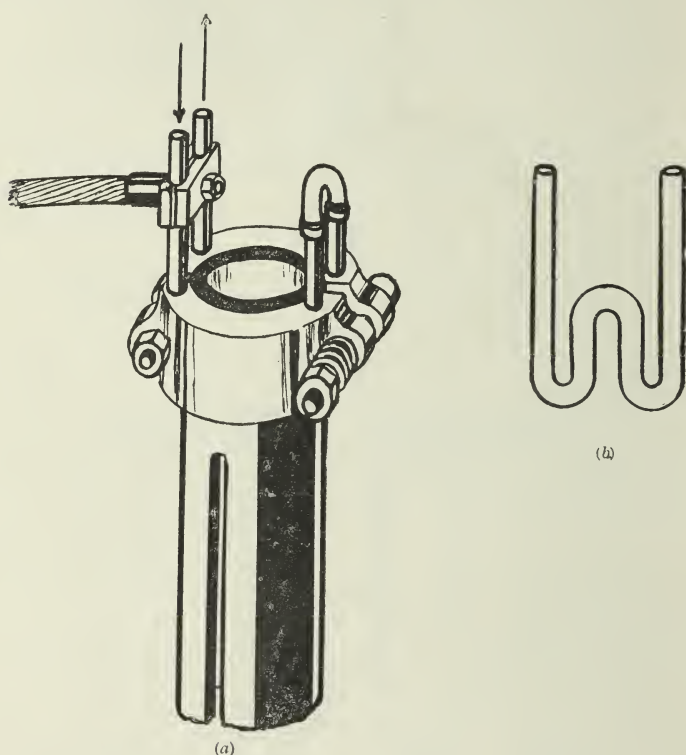


FIG. 3.—(a) One Electrode complete. Slot in Tube also illustrated. (b) Copper Tube before White Metal cast around.

Atmosphere within the Furnace.—During observations a steady stream of nitrogen is passed through the furnace, the inlet being near the window. This ensures freedom from dust and fog in the tube through which observations are taken and also produces a neutral atmosphere within the furnace.

With carbon tube or spiral furnaces it is of course necessary to provide a neutral or reducing atmosphere, otherwise the hot carbon is rapidly corroded away by oxidation. Hydrogen is not so satisfactory as nitrogen, since it readily diffuses through the hot walls without traversing the furnace.

Up to about $1,700^{\circ}\text{C}$. it is safe to assume that the atmosphere within the furnace is free from volatile carbon compounds. This is proved by the fact that pure iron contained in a magnesia crucible may be melted and heated to above $1,600^{\circ}\text{C}$. in the furnace without absorbing any carbon. At temperatures in the neighbourhood of $2,000^{\circ}\text{C}$. and above it is impossible to eliminate the possibility of contamination by carbon.

The atmosphere is highly ionized, and it has been shown* that currents of several amperes will pass between two insulated electrodes with an applied potential of only a few volts. The passage of the electricity is accompanied by the actual transport of material particles, probably molecular aggregates.

If a water-cooled tube is fixed through a furnace when at a temperature of about $2,500^{\circ}\text{C}$. it is possible to obtain a thick deposit of carbon sufficiently coherent to be slid off in short lengths. This phenomenon is accompanied by a flow of electricity from the hot carbon to the cooled tube without any applied e.m.f. At first a small positive current of a few micro-amperes, suc-

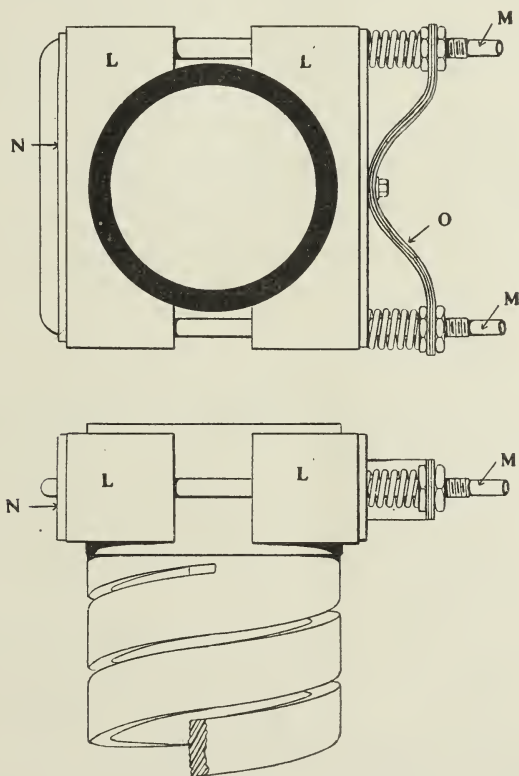


FIG. 4.—Electrode Design of Large Crucible Furnace.

ceeded as the temperature rises by a large negative current, the maximum amounting to 0.8 ampere, which afterwards diminishes to about 0.1 ampere, at which it remains practically constant. The positive transient current and the negative maximum are only obtained in the first heating of a new tube, so are probably due to the distillation of the silica and other impurities which are generally present in a new carbon tube to the extent of about 1 per cent. Consequently it is advisable to run a new tube to a higher temperature than the maximum it is desired to work to so as to free it from impurities.

This contamination of the contents when heated to temperatures

* Harker and Kaye, "The Emission of Electricity from Carbon at High Temperatures," *Proc. Roy. Soc., A*, vol. 86, p. 379, 1912.

exceeding $1,700^{\circ}\text{C.}$ is a serious limitation to the use of the carbon resistor furnaces, since the particles appear to be shot off from the walls with sufficient velocity to cover distances of at least several millimetres, possibly much more.

So far as the mere attainment of high temperatures is concerned, a carbon tube furnace is capable of $3,000^{\circ}\text{C.}$ for short periods.

Practically all commercial refractory bricks soften under loads at temperatures below $1,700^{\circ}\text{C.}$; consequently the contamination troubles only occur with such materials as pure zirconia. With the arrangement described, however, there is another source of contamination to be considered. It will be observed that the pressure is transmitted to the specimens by means of two carbon rods acting as plungers. When it is necessary to isolate the specimen from contact with carbon, distance pieces of metallic tungsten or other high melting-point metal must be employed.

Energy Control of the Furnace.—A general view of the auxiliary plant for the supply of energy to the furnace is shown in Fig. 5.

Alternating current is obtained from the motor generator set consisting of a motor (actually a rotary converter) coupled to an alternator of 15-kilowatt capacity. The voltage of the alternator is controlled by two field rheostats connected in series, one being conveniently located to the observer at the furnace. The current is transformed down by means of the transformer shown in the foreground of Fig. 5; currents of the order of 350 amperes being usual.

The Measurement of Temperature.—Temperatures are measured by means of a polarizing type of optical pyrometer. The sighting on the specimen is made in a slightly oblique direction, so as to avoid any possible error due to the temperature of the side of the specimen in direct line with the window being slightly lowered by radiation.

The temperature observations are effected by matching two adjacent fields of illumination, one due to the object, the other to an electric lamp, through which a constant current is passed. The temperatures are read directly on an engraved scale, over which the pointer attached to the eyepiece nicol moves. Temperature observations can be repeated within 10° at $1,500^{\circ}\text{C.}$ without difficulty.

The calibration of the instrument was effected by comparison with a thermo-couple under "black body" conditions, the couple being standardized by metal freeze-points. The freezing-points above $1,000^{\circ}\text{C.}$, on which the calibration is based are: Gold, $1,063^{\circ}$; copper (reducing atmosphere), $1,083^{\circ}$; nickel (neutral atmosphere), $1,452^{\circ}$; palladium, $1,549^{\circ}\text{C.}$

The melting-point of palladium marks the upper limit to which the gas thermometer scale has been carried: for the measurement of temperatures beyond this point the scale must be extrapolated on the basis of the radiation laws.

The optical system of this type of pyrometer is identical in principle with that of the König spectrophotometer, and consequently extrapolation on the basis of Wien's law is readily effected.

Specimens.—The results of the investigation into the behaviour of various materials under compression at high temperatures will be dealt with in a later paper, and here it will suffice to show a typical instance of the different behaviour of samples of two bricks, both of the same general class, magnesite, but differing in purity and firing temperature.

In Fig. 6, specimen A shows, for comparative purposes, the size of a specimen prepared for test; specimen B, the softening and deformation under-load of brick No. 1 at a temperature of $1,500^{\circ}\text{C.}$; specimen C, the

fracture without deformation of brick No. 2 at a temperature of $1,330^{\circ}$ C. Both were tested under the same pressure or about 30 lb. per square inch.

In conclusion, we take pleasure in thanking our director, Dr. Glazebrook, for placing the facilities of the workshop of the Heat Department at our disposal for the development of the design of this furnace.

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STAHLER and ELBERT : "Furnace," *Berichte d. Deutsch. Chem. Ges.*, vol. 46, p. 2070, 1913. Pressure furnace.

WOLF and MÜLLER : "Pressure and Vacuum Furnaces," *Zeit. f. Elektrochemie* (Halle), 20, pp. 1 and 177, 1914. In this furnace the jacket can be slid away from the tube. Joints at ends of jacket made by compressing discs of rubber between plates to expand them into contact with the internal walls similar to two pistons.

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MENDENHALL and FORSYTHE : "High Temperature Measurements with the Stefan Boltzmann Law," *Astrophysical Journ.*, p. 353, 1911 ; *Physical Review*, vol. 4, No. 1, July 1914. Describes a water-cooled furnace with reduced pressures inside.

ARSEM : "Vacuum Furnace," *Trans. Amer. Electrochem. Soc.*, vol. 9, p. 153, 1906 ; *Journ. Amer. Chem. Soc.*, vol. 28, p. 921, 1906.

YENSEN : "Vacuum Furnace," for melting pure iron and its alloys. Arsem type. *Electrician*, June 16, 1916 (see also vol. 75, 9, 119, 1915).

TUCKER : *Electrochem. and Met. Ind.*, vol. 5, 227, 1907.

NORTHROP : "A New High-temperature Furnace," *Mel. and Chem. Eng.*, January and May, 1914. Describes a graphite resistor furnace with conical electrodes. No details are given. Furnace designed for experiments on resistivity of molten metals.

NORTHROP : Series of papers, *Trans. Amer. Electro. Chem. Soc.*, 1911, 1914 ; *Journ. Franklin Institute*, 1913-16 ; *English Mechanic and World of Science*, June 18, 1916, and subsequent numbers.

FINK : "Vacuum Furnace for Ore Distillation," *Trans. Amer. Electrochem. Soc.*, 21, p. 445, 1912.

CALHANE and BARD : "An Efficient Electric Furnace for High Temperatures," *Met. and Chem. Eng.*, vol. 10, p. 461, 1912.

HANSEN : "Experimental Arc Furnace," *Electrochem. and Met. Ind.*, vol. 7, No. 5, p. 206, 1909. Laboratory form of arc furnace for metallurgical operations.

MALM : "High-temperature Experimental Furnace," *Met. and Chem. Eng.*, February 1915. Small arc furnace.

HUTTON and PETAVEL : *Journ. Inst. Elec. Eng.*, vol. 32, p. 236, 1903. Electrode holders for arc furnace.

HÄRDÉN : "Recent Development of the Kjellin and Rochling-Rodenhauer Electric Induction Furnace," *Trans. Faraday Soc.*, vol. 4, p. 120, 1908. An experimental 25-kw. furnace of this type is installed in the Heat Department of the National Physical Laboratory.

FITZGERALD : "A New Resistor Furnace," *Met. and Chem. Eng.*, 8, p. 317, 1910. Describes a novel type of furnace in which advantage is taken of the contact resistance between carbon bars to generate the heat. The bars have wedge-shaped cross-sections, and form the roof of the furnace ; one set with their edges up are supported by the side walls, while the others are dropped in between. Current is passed transversely across the bars.

THOMSON and FITZGERALD : "Radiation Resistor Furnace," *Met. and Chem. Eng.*, vol. 8, p. 289, 1910.

BOOKS ON ELECTRIC FURNACES.

(Dealing principally with Industrial Applications.)

MOISSON : "The Electric Furnace," trans. by Mouilpied, 1904 (Edward Arnold). Describes author's work with the arc furnace.

WRIGHT : "Electric Furnaces and their Industrial Application," new ed., 1910 (Constable).

BORCHERS : "Electric Furnaces," trans. by Solomon, 1908 (Longmans, Green & Co.). Useful reference volume : treatment not sufficiently critical.

KERSHAW : "Electro-thermal Methods of Iron and Steel Production, 1913" (Constable). Deals with electric furnace production of iron and steel. Review in *Trans. Faraday Soc.*, 1914.

STANSFIELD. "The Electric Furnace. Its Construction, Operation, and Uses," 2nd ed., 1914 (Mc-Graw Hill Book Company). A good introductory volume on the subject.

RODENHAUSER and SCHOENAWA. "Electric Furnaces in the Iron and Steel Industry," trans. by Baur, 1913 (John Wiley). Deals principally with induction furnaces. Review, *Trans. Faraday Soc.*, 1913.

BRONN : "The Electric Furnace in the service of the Ceramic Industry and in the Manufacture of Glass, Quartz, and its use in recent and important researches" (in German), 1910 (Wilhelm Knapp, Halle-a-S.). While electrical heating will undoubtedly be largely applied in future for the preparation and firing of refractory bricks and ceramic materials, the majority of the furnaces described in this book have scarcely advanced beyond the experimental stage.

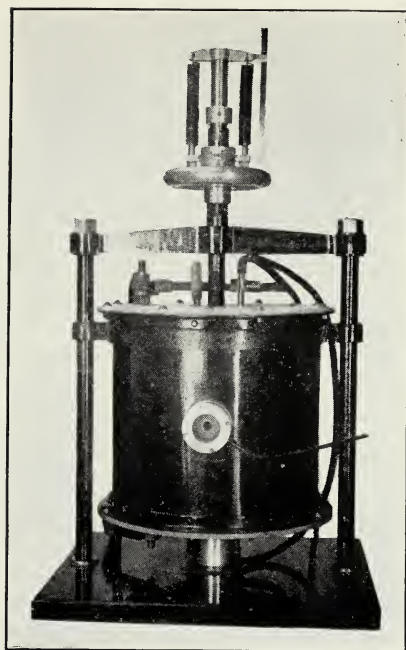


FIG. 1.—View of Furnace.

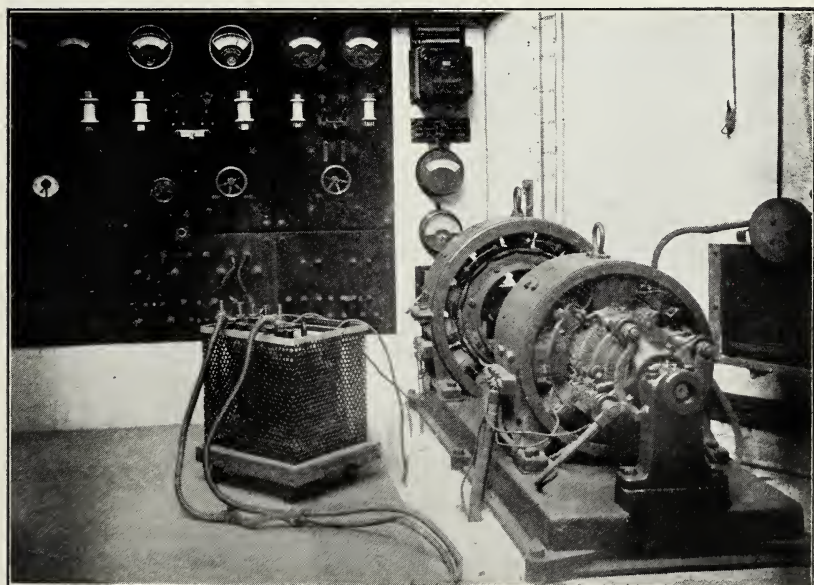


FIG. 5.—Motor Generator Set and Transformer for Energy Supply to the Furnace.
Frequency from 80 to 200 ; alternator with variable excitation giving a voltage up to 200 on slip-rings.
Ratio of transformer : 8 to 1 and 16 to 1.



A



B



C

FIG. 6.

REFRACTORIES.

Melting-points and Softening under Load.

KANOLT: "Melting-points of Refractory Oxides," *Bull. Bur. Stds.*, vol. 10, p. 295, 1914, and *Techns. Paper*, No. 10, 1912.

KANOLT: "Melting-points of Firebricks," *Trans. Amer. Electrochem. Soc.*, vol. 22, p. 95, 1912.

BLEININGER and BROWN: "The Testing of Clay Refractories, with special reference to their Load-carrying Capacity at Furnace Temperatures," *Techns. Paper*, No. 7, *Bull. Bur. Stds.*, 1912.

PARKER and HENSEL: *Trans. Amer. Cer. Soc.*, 7, 185, 1905.

BLEININGER and BROWN: *Trans. Amer. Cer. Soc.*, 12, 336, 1910; 13, 210, 1911.

BROWN: *Trans. Amer. Cer. Soc.*, 14, 391, 1912.

HERAEUS: *Zeit. angew. Chem.*, 18, 49, 1905.

HOFMAN and DEMOND: *Trans. Am. Inst. Mining Eng.*, 24, p. 42, 1894.

HOFMAN and STROUGHTON: *Trans. Am. Inst. Mining Eng.*, 28, p. 440, 1898.

HOFMAN: *Trans. Am. Inst. Mining Eng.*, 25, p. 3, 1895; 28, p. 435, 1898.

GARY: *Mitt. k. tech. Versuchsanstalten*, 14, p. 63, 1896.

JOCHUM: *Thonindustrie Zs.*, 27, p. 764, 1903.

WEBER: *Trans. Am. Inst. Mining Eng.*, 35, p. 637, 1904.

MELLOR and MOORE: "The Effect of Loads on the Refractoriness of Fire-clays," *Trans. Eng. Cer. Soc.*, vol. 15, p. 117, 1915-16.

NESBITT and BELL: "Practical Methods for Testing Refractory Fire Brick," *Met. and Chem. Eng.*, August 15, 1916.

RUFF, SEIFERHELD, and SUDA: "Fusion and Volatilization of Refractory Oxides in the Electric Vacuum Furnace," *Zeit. Anorg. Chem.*, 82, p. 373, 1913.

WATTS and MENDENHALL: "Softening of Carbon at High Temperatures," *Phys. Rev.*, vol. 33, p. 65, 1911.

Electric Furnace Products.

GOODWIN and MAILEY: "Physical Properties of Fused MgO," *Trans. Amer. Electrochem. Soc.*, vol. 9, 1906. Describes fusion of MgO in carbon tube furnace.

MEYER: "Refractory Properties of Zirconia," *Met. and Chem. Eng.*, December 1914, April 1915.

RUFF, SEIFERHELD, and BRUSCHKE: "Preparation of Refractory Objects of Zirconium Dioxide," *Zeit. Anorg. Chem.*, 86, p. 389, 1914.

BÖHM: "The Technical Application of Crude Zirconia," *Chem. Zeit.*, 35, 1901, 1911.

BÖHM: "Alundum and Graphite," *Scientific Amer. Suppl.*, No. 1499, September 24, 1904.

JACOBS: "Alundum," U.S.A. Patent No. 659, 926 (1900).

WEDEKIND: "Synthesis of Borites in the Vacuum Electric Furnace," *Ber. Deutsch. Chem. Ges.*, p. 1198, 1913.

FITZGERALD: "Carborundum, CSi," Engelhardt Monographs on Applied Electrochemistry (in German).

FITZGERALD: *Fourn. Frankl. Inst.*, 143, p. 81, 1897.

FITZGERALD: "Carborundum Furnace," *Electrochem. and Met. Ind.*, vol. 4, p. 53.

ACHESON: *Fourn. Frankl. Inst.*, 136, pp. 194 and 279, 1893.

RICHARDS: "Carborundum Manufacture," *Electrochem. and Met. Ind.*, vol. 1, p. 50, 1902; vol. 7, p. 189, 1909.

TUCKER and LAMPEN: "Carborundum," *Journ. Amer. Chem. Soc.*, vol. 28, p. 853, 1906.

GILLETTE: "Carborundum," *Journ. Phys. Chem.*, 15, p. 275, 1911. Physico-chemical study of formation.

BANCROFT, WALKER, and MILLER: "Study of a Small Carborundum Furnace," 8th International Congress of Applied Chemistry, Electrochemistry Section, 1912; *Trans. Amer. Electrochem. Soc.*, 22, p. 73, 1912. (Experiments on the yield of a furnace as affected by length of run.)

SAUNDERS: "Carborundum," *Trans. Amer. Electrochem. Soc.*, 21, p. 425, 1912.

BÖLLING: "Silundum (CSi)," *Electrochem. and Met. Ind.*, 7, p. 25, 1909. Can be used as resistors: prepared by exposing rods of carbon to silica vapour.

TONE: "Silicon," *Electrochem. and Met. Ind.*, 7, 192 (1909), vol. 2, p. 111; vol. 4, p. 464; vol. 5, p. 141. Preparation in arc furnaces using sand and coke.

RICHARDS: "Silicon and Boron," *Scientific Amer. Suppl.*, Nos. 2058, 2059, June 12 and 19, 1915.

DESPRETZ: *C. R.*, 89, p. 720, 1849. This paper is of historical interest. When a carbon rod embedded in sand was heated electrically to a high temperature, a hard tube about six times the diameter of the rod was obtained. It is probable that carborundum crystals were formed, although Despretz did not realize the fact.

TUCKER: "Manufacture of Silicon in a Small Laboratory Furnace," *Met. and Chem. Eng.*, 8, p. 19, 1910.

ACHESON: "Graphite, its Formation and Manufacture," *Journ. Frankl. Inst.*, pp. 147 and 475, 1899.

RICHARDS: "Graphite Manufacture," *Electrochem. and Met. Ind.*, vol. 1, p. 52 (1902).

FITZGERALD: "Acheson Graphite Furnace," *Electrochem. and Met. Ind.*, vol. 3, p. 416; see also vol. 7, p. 187 (1909).

ACHESON: "Researches on Electric Furnace Products," *Trans. Faraday Soc.*, vol. 7, p. 217, 1911.

ARSEM: "Transformation of other forms of Carbon into Graphite," *Trans. Amer. Electrochem. Soc.*, vol. 20, p. 105, 1911.

FITZGERALD: "Artificial Graphite," vol. 15 of the Engelhardt Monographs.

VOGEL: "Quartz Fusion Furnace," *Electrochem. Zeit.* (Berlin), pp. 121, 181, and 218, 1911.

TONE: "Silicidized Carbon—Silfrax," *Trans. Amer. Electrochem. Soc.*, 26, p. 181, 1914.

WEINTRAUB: "Fibrox," *Trans. Amer. Electrochem. Soc.*, 27, p. 267, 1915.

NORTHROP: "Properties of Fibrox," *Met. and Chem. Eng.*, 15, p. 409, 1916.

SOSMAN: "The Common Refractory Oxides," *Journ. of Ind. and Eng. Chem.*, November 1916, p. 985.

DISCUSSION.

Mr. H. M. Ridge said he had never yet been able to obtain an apparatus which could be subjected to 1,500 or 1,600 degrees Centigrade and would at the same time give accurate tests of what compression strains firebrick materials would stand, and from this point of view Mr. Griffiths' furnace would give valuable results. Had Mr. Griffiths made comparative tests of a number of samples from the same brick, and if so within what percentage of accuracy did the results agree? Also, could Mr. Griffiths give any results obtained on what might be looked upon as standard bricks obtainable in this country—for instance, from South Scotland, Leeds, Stourbridge, and Wales? Perhaps if comparative tests of a number of samples had been made they might be published. The results would be of very great interest. Further, what was the risk of breakdown of the carbon rods in the furnace? The effect of the recent regulations of the Ministry of Munitions fixing the maximum price for firebrick irrespective of quality had been that makers of the best bricks were unable to raise the prices, whereas those who made inferior bricks had increased their prices considerably. He had wanted several hundred thousand common firebricks for work for which a low-class firebrick would do well, and he was asked prohibitive prices for them, yet the Ministry did not see their way to fix the price according to quality, on account of the difficulties of testing. If this apparatus could be brought into general use, therefore, it would be possible to determine the strengths and fire-resisting qualities, and upon these to fix a sliding scale for the maximum prices.

Dr. H. C. Greenwood asked as to whether tests on the effect of temperature on the tensile strength of the bricks had been carried out. This must have some influence on the cracking of refractories, in cases where the material is subjected to tension, e.g. by stresses set up in the under side of retorts supported only at intervals, by contraction on cooling, etc.

Dr. H. Borns asked how long it took to make a test, and how it was conducted. The result would obviously depend upon the rates of putting on the pressure and of raising the temperature. Were the specimens tested under different conditions, and were the results of similar tests fairly concordant? The literature list at the end of the Paper might be supplemented.

Dr. R. Lessing asked whether it would be possible to use larger test pieces in Mr. Griffiths' furnace. He recognized that the testing of full-size bricks, as it was done, for instance, by Bleininger at Pittsburgh, was attended by the difficulty of raising the whole mass of the brick to a uniform temperature.

The size mattered little where homogeneous clays or fine-grained mixtures are examined, but in the case of refractories made with large-grained grog, it was important to have a sufficient number of granules of grog included in the test piece. He also drew attention to the work recently done by Mellor and Moore in which a modified Hirsch furnace was used.

Dr. W. Rosenhain said that the method of testing refractories under compression involved a point which required careful attention in order that the meaning of the test might be fully appreciated.

The failure of a test piece under compression, particularly if the pressure used was at all heavy, might not in the least mean that the material had melted, or had even approached melting. The majority of substances became weaker with rising temperature, and failure might occur under com-

pression by an ordinary shear fracture, not involving even incipient fusion. If this point of view were borne in mind, one would not be surprised to find that the temperature at which fractures occurred were very different from those at which a cone of the material would melt down in the ordinary way.

Further, all the difficulties which applied to compression tests in the ordinary way would also apply to this test. The influence of ratio of length to diameter of the test piece must be considered, and also the difficulty of keeping the surfaces between which the test piece is compressed exactly true. It would also be necessary to have the end surfaces of the test piece itself flat and parallel to a considerable degree of accuracy. The manner of applying the load is also of importance, since any looseness of the graphite pieces, through which the compression is transmitted, might easily lead to one-sided loading of the little test piece. He had no doubt that in the hands of Mr. Griffiths, and with the appliances available at the National Physical Laboratory, these difficulties had been overcome and could be consistently avoided, but the method was one which it would not be easy to apply in ordinary circumstances.

The Authors, in reply, stated that specimens were taken from various parts of a brick and concordance of results was expected for each sample.

Concerning data for bricks from different localities, sufficient information on this point had not been determined up to the present owing to pressure of other work.

The carbon rods had given no trouble.

Tensile strength experiments had not yet been attempted; industrially there did not appear to be any demand for such tests, although the results would undoubtedly be of interest. Usually the experiment took $2\frac{1}{2}$ hours at a rate of increase of temperature of about 10° per minute.

The pressure was maintained constant at a predetermined value throughout the experiment: tests at several pressures were customary.

They were greatly obliged to Dr. Borns for supplementing the list of references.

In reply to Dr. Lessing, the authors stated that they had doubled the dimensions of the test piece in some experiments. The dimensions were kept small to ensure uniform distribution of temperature in the specimen; they saw no point in testing a full-size brick, since the results obtained with the apparatus were representative for any particular brick from which the specimens were taken. To carry out such tests would involve a very large apparatus.

Most of the experiments hitherto made had been carried out on fine structure material, and they had not encountered the difficulty concerning the size of grog granules mentioned by Dr. Lessing. References to the work of others in this field were given in the paper.

Dr. Rosenhain's remarks, of course, referred to cases of fracture by shear and did not apply to softening-point determinations.

Generally when a refractory failed by sudden crushing, under light load, without incipient fusion, it suggested that the method of manufacture had not been carried out properly, since in many cases the effect appeared to be due to the volatilization or combustion of the binder employed, which probably would not occur if the brick had been fired at a sufficiently high temperature to produce vitrification. The authors did not believe that fractures such as that shown by C Fig. 6 had any relation to the gradual weakening of substances with increasing temperature, as the magnitude of the load in these experiments was small: a brick at room temperatures will withstand stress of the order of 2 tons per square inch before crushing.

With regard to the question of the ratio of the length to the diameter, this point had been carefully considered and standard engineering practice followed.

The precaution necessary in applying the load was to allow the top rod to take up its own position before bringing the plunger into contact with it. They quite agreed with the remark that the method of testing refractories under load was one which required some care and well-constructed apparatus, since reliable compressive tests on materials were difficult even at room temperatures.

Replying to Sir R. Hadfield, they stated that the furnace had been designed for test work in the laboratory.

One point which had not been referred to in the discussion, to which they desired to draw attention, was the fact that materials frequently withstood higher temperatures when one face only was exposed to the heat than would have been anticipated from the softening-point. This appeared to be due to the temperature gradient through the material maintaining the body of the brick at a lower temperature than the face: under such conditions the softening-point under load could be exceeded for the face temperature. Any attempt at thermal insulation of such a furnace by the addition of lagging generally resulted in failure of the refractory lining.

The following written Communications to the Discussion were received—

Mr. W. Donald (Glasgow) wrote expressing his regret at being unable to be present at the discussion, but it gave him pleasure to send for exhibit on behalf of the Eglinton Silica Brick Company samples of the following :—

1. Raw Magnesite as received from the Greek mines.
2. Calcined Magnesite.
3. Magnesite Cement when it is ready to be moulded into brick form.
4. Magnesite Brick, size $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ in., made from pure Greek magnesite.
5. Magnesite Brick, $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ in., made from Greek magnesite with the addition of 4 per cent. of iron oxide and fired at the same temperature.

In the past, magnesite bricks have been most largely made in Austria, but since the beginning of the war the supplies of magnesite have almost exclusively come from Greece, and they were devoting themselves to the production of Greek magnesite bricks and doing everything possible so as to produce bricks equal in quality to the Austrian bricks. The addition of the iron oxide was made so as to try to approximate in analyses to the Austrian magnesite. These two magnesites analyse approximately as follows :—

	Greek.	Austrian.
MgO	88.0	83.0
CaO	5.0	4.0
Al ₂ O ₃	1.0	3.0
Fe ₂ O ₃	0.5	8.0
SiO ₂	5.5	2.0
	100.0	100.0

It was found by all concerned that the Greek magnesite was too pure and that the addition of the extra percentage of silica gave the brick too great a silica content, but that the natural addition was the iron. So far as the fusion-point was concerned, it seemed in no way to be seriously affected. On the other hand, it seemed to give a very much greater binding strength to the particles without in any way taking from their refractory qualities.

The following further samples were also exhibited :—

1. Chrome Ore as received at the steamer from India or Rhodesia.
2. Chrome Cement from which the bricks are manufactured.
3. Chrome Brick, $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$ in.

They were at present only interested in furnace linings for basic steel furnaces, and if he might make a suggestion it would be that the question as to the use of dolomite for basic steel furnaces in conjunction with magnesite bricks should be seriously considered. It is well known that the American steelworks prefer to use magnesite cement and that they have their own methods for making this, which is more suitable than they have ever found dolomite to be.

Magnesite bricks are used in basic steel furnaces to form the foundations and are generally lined in this country with about 14 in. of dolomite which has been carefully rammed in, and often fritted in, in layers of 3 in. Steel-

makers often noticed that this rammed dolomite boils with the metal, and they are at a loss to understand what one can mean by the term "bad dolomite" when this does happen. From observations we have made we beg to offer the suggestion that ferrates of lime are formed, and that these are very active under certain conditions. What we have not been able to form a definite opinion about is as to whether ferrates of magnesia are also formed, but from statements that have been made to us by those acquainted with the American steelworks we have formed the opinion that magnesite cement, which is so largely used in the United States, does not act in the way that dolomite does in this country, and that, therefore, ferrates of magnesia do not boil in the way that ferrates of lime seem to do. When dolomite boils in this way it seems to have a very destructive effect on the magnesite bricks in the foundation of the furnace. Again, with the use of dolomite there is constant need of fettling the furnace, and there is necessarily loss of heat while this is being done. If the methods in use in the United States were attempted in this country it might be found possible to effect a great saving in the time that is at present lost in the furnaces, and that might amply repay for the extra cost of the magnesite in comparison with dolomite.*

With a view (a) to improve the quality of magnesite, chrome, and silica bricks; (b) to fix a standard of quality embracing the highest grade of physical and chemical properties desirable in the refractories used in basic and other furnaces; and (c) by producing the finest grade of these highest refractories to make the iron and steel manufacturers independent of supplies of German and Austrian products in the future, they had recently proposed to the Iron and Steel Institute that (1) a standard of refractoriness, density, porosity, crushing resistance and thermal coefficient should be set up; (2) this standard be used by all makers of refractories and be stipulated in contracts by iron and steel smelters; (3) the standard to be set up by Dr. J. W. Mellor in consultation with representatives of the iron and steel industries and makers of refractory bricks.

In view of the great developments in electrometallurgy that he was confident would follow the conclusion of peace, he felt sure the Faraday Society would be interested in this matter. As an indication of what might be possible, he begged to point out the situation in Serbia, which, while a small country, had considerable mineral deposits and a splendid supply of water power for the generating of heat in electric furnaces. If it were possible to develop such natural resources one might see shipbuilding taking place on the Danube, particularly in view of the great developments that are bound to take place if the Black Sea is more open than it has been in the past to shipping.

They themselves were giving very close attention to the linings of electric furnaces, and they hoped very soon to put before the makers of electric steel special brick for their consideration.

(Note added January 15, 1917) Since writing the above, information which

* Several firms in this country have used magnesite cement in place of dolomite, and so long as the metal was cold this was very serviceable. When, however, the metal was poured into the steel furnace direct from the blast furnace the magnesite cement would not bear the weight of the pouring molten metal any better than dolomite would, and was even more difficult to fettle sometimes than the dolomite was. This, however, has been reported to us not to have been the experience in the United States. In this country attempts were made to use magnesite cement that was mixed with about 5 to 10 per cent. of basic slag. An indication that has come to us about two successful trials elsewhere is that Austrian magnesite containing only 82 per cent. of magnesia was mixed with about 20 per cent. of basic slag, and this gave a satisfactory cement quite able to withstand the action of the molten metal.

I have received leads me to think that while in America dolomite cannot be used to advantage in conjunction with magnesite bricks, this probably does not apply to the treatment of the iron ores which are available in this country.

Dr. A. B. Searle (Sheffield) wished to support the statements which had been made to the effect that chemical analysis was secondary in importance to some of the physical characters of firebricks. He had for several years made a practice of relying chiefly on physical and microscopical methods for all materials used in firebrick manufacture and had given reasons for this in several papers he had published, and particularly in his book *Refractory Materials: their Manufacture and Use*.*

The petrological method of examining refractory materials which was so well described by Professor Fearnside was by no means as new as might be supposed, though very little work on it has been published in this country. He (the speaker) had found it in extensive use in Germany in 1900, and had employed it frequently since. One of the best methods he knew for ascertaining whether a silica rock would make satisfactory bricks was to examine it microscopically before and after treatment with suitable stains, as proposed by Wernicke in 1899.

The desire for co-ordination had been repeatedly expressed that evening, but to secure this it is necessary to have some medium of communication equally accessible to all concerned. He suggested that the manufacturers of refractory materials were particularly fortunate in the possession of a trade paper which devoted special attention to the scientific and technological sides of the matter. If some academic investigators would pay more attention to trade journals, a large amount of the present overlapping and repetition of experimental work would be avoided and the co-ordination of the manufacturers, users, and independent investigators would be more readily achieved.

Much of the apparent indifference among manufacturers of refractory materials was due to two causes: (a) most of the firms concerned were small, with very limited capital, and so were unable to expend large sums on research or even to make sufficient use of such research when published; and (b) some of the more progressive firms had been very unfortunate in the scientific work done for them by students fresh from college and by other chemists who were devoid of practical manufacturing experience. It was a realization of the fact that most of the manufacturers of refractory materials were unable to maintain a scientific adviser for their exclusive use which had caused him to start in practice in 1901. His leading clients had assured him that the progress they had made fully justified them in combining to maintain a central testing station and technological bureau dealing solely with clays, sands, and their products. He looked forward to the time when other manufacturers would not be content with researches carried on in State-aided colleges and schools by men whose chief occupation should be educational, but would employ specialists who devoted their lives solely to the investigation of technical problems. This was the method used so successfully in the development of the refractories industries in Germany, the ablest investigators being retained by a firm or by a group of firms, so as to investigate thoroughly all the problems arising in connection with these firms, and the few manufacturers in this country who had for some years combined and adopted this method were convinced that it was the right one. It was

* This volume was announced for publication three months ago, but unfortunately an extensive fire at the printer's has destroyed most of the type, so that the whole is now being re-set.

free from the uncertainties of grants from the State ; it ensured that the whole of the money was spent on problems of a practical character, and it gave the benefit of all discoveries to those who were most entitled to them. It left the Universities free to concentrate on questions of academic interest—for which they were specially fitted.

The analogous problem had been satisfactorily solved in the Portland cement industry by similar combinations of manufacturers, with complete success so far as they had gone, though much more remained to be done. The Brown-Firth Research Laboratory was another example, taken from the steel industry.

The difficulty of "ways and means" is much smaller than was commonly supposed, and the savings effected in fuel and in other ways far exceed the cost of maintaining a well-equipped laboratory and testing station.

Mr. T. Allen (Dudley) wrote regretting his own and Mr. Gibbons's inability, on account of illness, to attend the meeting, which they were exceedingly sorry to miss. The subjects to be dealt with were of great fascination and interest, and particularly to their firm, who, he stated with all modesty, had done their best, regardless of cost, to improve the quality of their manufactures during the last five or six years. The result of their initial efforts might not have been all that could be desired, and he did not suppose that this remark applied particularly to any individual firm. Some adopted greatly altered methods of manufacture, and the difficulty of realizing the results was considerable. When one concedes that it sometimes takes years to prove the value or otherwise of a change in the manufacture of a retort, this difficulty is apparent. Laboratory tests may show excellent results : the writer recalled tests made on material in the early days of the Standard Specifications, and taking a period of six months, refractory tests were made over cone 32 and contraction tests were down as low as 0.50 per cent., and were practically constant for months. These results, however, did not necessarily mean that in actual practice the best retort was produced, but manufacturers had to thank the Refractory Materials Committee, in conjunction with Dr. Mellor, for the excellent work they had done, and for the lead and encouragement they had shown to all from time to time. He was convinced that at any rate some manufacturers were now working on the right lines, and that the materials produced were more adapted to meet the exacting conditions of present-day carbonization than they had ever been. The value of, say, a retort should be based not particularly on its life (he thought perhaps too much had been made of this in the past), but upon actual results in weight of coal carbonized, fuel consumption, etc. Refractory materials were now called upon to do much greater duty in lesser time, and particularly so in retorts which had to stand the wear and tear of modern stoking machinery. The late Mr. G. Gibbons got out a diagram some few years ago which appeared to prove conclusively that there was no economy in running a retort more than, say, 10/1,200 days. Reduced make of gas, reduced quantity of coke for sale, and extra fuel required to burn off charges in old retorts, are so important a set of factors, especially with the present value of coke, that the cost of renewals is not of such importance as is generally believed.

As to the supposed higher value of German retorts and American silica material, would it be out of place to ask if Germany or America can show us any installation that produced, in regard to make and quality of gas, throughput of coal, coke available for sale, and used as fuel, and relative cost per ton of coal carbonized, better results than were shown by, say, modern

London or some of our large provincial installations? He doubted very much whether they could do so. After all, it was largely a question of financial results, and in judging refractory materials all round results should be considered.

Mr. F. Dransfield (Oldham) wrote as follows:—

It occurs to the writer that the manufacturing and commercial side of the subject might be more fully treated with a view to inducing manufacturers to adopt more uniform methods in the production of these essential commodities, and I believe the recent Geological Survey has this for one of its objects.

Another important matter for consideration is the enormous wastage and deliberate loss of refractory clays lying under the coal seams—particularly in the lower coal measures, such as the lower mountain mine seam—by the winning of the coal only, the consequence being that the clay cannot afterwards be won, owing to the bad state of the roof making it both too dangerous and too costly an enterprise.

Such a valuable and necessary commodity ought to be carefully reserved in view of the gradual exhaustion of the known material, and, as far as possible, the coal and clay should be mined together. This of course could only be attained by legislation, and I do not know whether my remarks come under the scope of the operations of your Society, but they certainly have a bearing on the production of refractory materials essential to the future welfare of the iron and steel industries of the country.

In and around this district alone the coal has been won from innumerable pits and, with very few exceptions, the ganister or mountain mine clay has been left behind over a great area, and many thousands of acres of highly refractory clays practically lost.

Mr. Alleyne Reynolds (*communicated November 9, 1916*): I came away from the meeting with a sense of elation at the spirit manifested in all the utterances I had been an intent listener to. It is now eighteen years since I had actual charge of an important battery of acid open-hearth steel furnaces, the output of which was largely munitions. My mission since then has been a private one in connection with a search for still better methods of producing large and small steel ingots and castings. One of the first requirements is to obtain better refractories, the other to improve furnaces within the limits that present-day refractories permit of. In consequence of having seen nothing like serious attempts made by my fellow-Britons to equal the zeal of Germanic peoples regarding refractories, especially a certain great Austrian steelworks, I have, on stating the fact in pre-war days, often been rather insultingly accused of being pro-German. I have no compunction in saying that, considering that in these Austrian works clamped arches of silica bricks, as much as 8 feet in width, have been employed for more than twenty years within my personal knowledge, it is a disgrace to us as an unsurpassable nation to allow a continuance to exist of the production of silica bricks with something approaching 20 per cent. expansion. This same Austrian firm has devoted more attention to heating their ladles properly, and above all making ladle nozzles of the proper shape and quality, than any British firm within my not very varied or extensive knowledge as a specialist. This great Austrian firm, with its unhemmed-in works, met the difficulties concerning refractories by manufacturing them themselves.

Our steel-makers must do the like by co-operation with the makers of refractories. This will not come about so long as they are so frightened of, say, a brickmaker conveying "secrets" of steel manufacture from one works to another. As a matter of fact, even an expert steel-maker can learn

very little worth knowing from seeing another's manufacture carried out *unless he is told why so and so is being done*. I would not be frightened of any brickmaker discovering any "secret" of mine by seeing my work for months continuously, nor do I other than assume that most of my "secrets" have been independently evolved by others who keep them secret. Undoubtedly Sir Robert Hadfield has been far and away the most generously communicative expert British steel-maker, and I attribute the large dividends paid by his well-run company to that fact. If you give no information away you must not expect to receive any gratis. That gentleman's large-minded scientific spirit is bound to reflect itself beneficially on the commercial as well as technical side of a business guided in its destinies by him. A comment made to me in the hall was to the effect that the subject of refractories seemed rather outside the scope of the Faraday Society. Considering that no known refractory bricks fulfil at all adequately the demands of a regenerative gas-fired furnace, it seems to me that the fringe of the requirements of the electric furnace has hardly been touched, and until it is more than touched the Faraday Society's major sphere can hardly make great progress. A jocular remark made by my father (the late Edward Reynolds) some thirty-five years ago may be of modern interest. He was showing some visitors round the works, and included amongst them was a typical cheery British clergyman. On coming to the steel-melting furnaces, he asked my father if "Nebuchadnezzar's furnace when heated seven times its wont was heated seven times as hot as those he was looking at." To this my father replied that if it were, he would like to know where Nebuchadnezzar bought his bricks. In his opening address the President touched upon the subject of steel-casting ladle nozzles, on which subject a small volume would be required to contain the full considerations to be dealt with. It is a subject to which I have devoted special attention. It is not the slightest use to fill a ladle with perfect steel unless one knows how to cast it into the mould properly. For the benefit of non-steel-maker members of this Society it will be relevant to this discussion to touch on this subject. If a chill mould is filled too quickly the shell of steel formed by the chilling action of the mould is burst by the pressure due to the head of molten metal. If the stream from the ladle be not clean, steady, and central, an unsound ingot must be produced. The ratio of mould surface to volume of ingot decreases as the volume of latter increases, and to secure a steady compact stream a relatively smaller nozzle is required, the larger the section of the ingot, as it is unavoidably necessary to run the stream full bore through the nozzle, except when "feeding" the cast ingot. If then the nozzle wears substantially, the ingot must be defective. If the plug stopper does not fit the nozzle, there must be fatal dribbling, and if one presses the stopper down hard when softened by heat, it and the nozzle weld together. The skilled "plug-runner" then keeps opening and closing the nozzle, dropping some splashes of steel on the foundry floor, in between casting each of a plurality of castings from one ladle. In my managerial days I used personally to cast the ladles occasionally, in order to "feel" the quality of the stoppers and nozzles, and in the case of exceptionally numerous and tricky castings, used to cast them myself. As a side issue, I venture to disagree with Sir Robert Hadfield as to worn clay nozzles accounting for slag inclusions in steel ingots. These slag inclusions are, in my opinion, caused by segregation, and are generated by actually reciprocated reactions on the dissolved FeO and FeS of not perfectly produced steels. The slags produced by reaction on fire-clay nozzles are, I am confident, floated up out of the molten metal. I should be much more suspicious of a steel ingot cast through a magnesite nozzle. I should fear that minute decrepitated particles of

magnesite would be carried into the mould and remain in suspension in the steel as an emulsion.

In my opinion the troubles occurring with ladle nozzles and stoppers are little due to real lack of refractoriness therein. Precisely similar and no more refractory materials are used for crucibles in which steel is melted. In both cases the contact surface of the refractory with the steel is reduced in refractoriness by being brought into chemical equilibrium with the steel. In the case of the nozzle, this surface is mechanically washed away, as soon as formed. One may at once diagnose manganese as the main, and iron as the subsidiary elements bringing this about. Per unit oxygen involved, basic manganous oxide and acid silica have almost exactly equal heats of formation, whilst basic ferrous oxide has a less heat of formation. Thus, as in dead melting crucible steel, manganese and iron reduce silica, to form silicates and silicides, and neutralize the surface of the acid refractory, thus glazing it. It is for the reason of the equality of heats of formation of silica and manganous oxide that it is so easy to produce carbon-free silicide of manganese.

Plumbago is attacked by a similar reaction. Acid clay bond is attacked and fluxed away, thus exposing particles of true plumbago to the action of molten iron, which it carbonizes, thus exposing its rear wrapping of bond to reduction, and thus, by alternating actions, erosion occurs. In crucibles made of plumbago, the cutting of the crucible, and the substantial carburization of the steel, is practically confined to the slag line, where the slag is able to remove the neutralized clay by dissolving it.

The President did not receive the support I expected to find in regard to his contention that samples of refractories should be properly analysed. He did not suggest that other precautions should not be taken if this were done.

Twenty years ago I found out that in some cases I had not tested firebricks properly, and had unfairly condemned some brands for certain purposes.

I used to place samples of best standard bricks and proposed substitutes in one of the gas-fired crucible furnaces, and subject them to destructive fusion temperature. This was a correct first test for bricks to be subjected to oxidizing atmospheres, but not a comparative test for reducing atmospheres, and what method should be adopted must be decided by a preliminary rather complete analysis. Fe_2O_3 and Fe_3O_4 seem to increase the refractoriness of firebricks exposed to oxidizing atmospheres, and any form of iron oxide is detrimental to bricks subjected to reducing atmospheres. Iron pyrites is of little detriment in the latter case, and very detrimental in the former. The reason is identical. FeO is a powerful flux, which must not be produced by reduction of higher oxides, or oxidation of sulphides. Traces of FeO may only beneficially glaze the brick and be roasted into higher non-detrimental oxides.

Mr. Johns' experiences in regard to magnetite formed in "seasoned" silica bricks confirm my own.

I was rather astonished some time ago at learning from one of our greatest chemists that there was no real analytical method of quantitatively ascertaining Fe_3O_4 included in silicates. One depends on making intelligent guesses based on the figures given by the analyst for FeO and Fe_2O_3 .

Fe_2O_3 seems to behave in regard to SiO_2 and FeO analogously to Al_2O_3 .

It is a significant fact that the bricks forming the regenerators of open-hearth furnaces take up considerably more iron in the gas than the air chambers. In the former I have known bricks increase in weight something like 20 per cent., and to pick up sometimes even 30 per cent. of iron

with little alteration of dimension. Their regenerative efficiency is increased thereby. This subject alone, properly investigated and considered, would provide material for a small volume.

Another subject on which a volume might be written is the volatilization of refractories, in particular magnesite, at relatively low temperatures such as 1,300° C. when the conditions are fully reducing. It is generally due, I believe, to catalytic actions, but is so common that it caused me to finally abandon all attempts to solve the problem of producing better steels by evolving an electric furnace fulfilling what in my opinion are the essential conditions demanded to meet the metallurgy of steel.

In conclusion, I should like to emphasize my opinion that the President and Council of the Faraday Society are deserving the thanks not only of its lay members, but of the nation, for taking up the promotion of the giving of adequate attention to a matter of burning national urgency. It is the spirit shown by them which is essential to winning the war in a military sense, and the "war after the war" as a manufacturing community.

Much of the sacrifices made prove not to have been made in vain by this stirring up of scientific national pride, which was required. I have always felt my fellow-Britons could beat the Germanic peoples if only they would not exhibit those signs of degeneration which led certain types of men to style me pro-German for my patriotic urging of Germanic thoroughness.

Mr. C. H. Sankey, in a communication sent in after the meeting, wrote that the success of the meeting must have afforded the Society great pleasure. He was most interested, and enjoyed the President's opening address especially. He had been connected with and interested in the firebrick trade for many years, and he had been appalled to find how little the majority of the large firebrick-makers knew about their own clays. The absence of any desire to change or improve what they had supplied in a haphazard way for many years was most marked.

His firm had occasion to write to a large firm of manufacturers, who had raised for at least thirty years large quantities of an excellent stoneware clay. Besides manufacturing various articles themselves, they had also supplied the clay to other manufacturers, and on asking them to furnish analyses of their clays they told him they had never had an analysis taken.

Another firebrick-works, who had supplied Germany with regular cargoes of fire-clay, on being asked for samples of the material, informed him that they only worked the seam for the clay they sent abroad, and made no use of it themselves. He had an analysis of the clay, and was quite satisfied that it was a more valuable clay than the one they were working, and this the Germans knew very well. It seemed most extraordinary that the clay, which was very rich in alumina (which Germany no doubt appreciated), was only shipped abroad to come back, without doubt, in the manufactured article.

It is in this way that the Germans before the war were taking orders from our own English makers in this country by their more scientific methods of blending, etc.

With regard to the analysis of firebricks, he was surprised at one speaker having made analyses of two quite different fire-clays, and although he gave the analyses as being identical in every particular, yet he stated one brick proved to be good and the other bad, and could not explain the reason.

To the writer's mind it just proved the very point he wished to emphasize, and which seemed to be the cause of a great deal of the trouble in an

analysis. To give only the percentage of silica, without stating how much of it is in a *free* state and how much in a *combined* state, was altogether insufficient and misleading. If the analysis had been complete, it would have helped to explain the cause of the two bricks giving such opposite results in practice. Often when inquiring as to the amount of *free* and *combined* silica, the manufacturer has been bewildered, and in only a few cases has understood the meaning. He contended that both free and combined silica should be stated for an analysis to be of any use, and it would also at the same time throw light on the physical construction of the brick.

As regards silica bricks, the writer personally made very pure silica firebricks, of which a fair quantity were sold successfully. They had the unique property of being free from expansion and contraction, both in the manufacture and in after-use. The bricks could be made to any density and specific gravity, from 1 ton to 3 tons per 1,000.

Mr. Arthur A. Knox (Glenboig) (*communicated November 23, 1916*): I have read the discussions on refractory materials with considerable interest, and being connected with the firebrick industry in a technical capacity it is with much pleasure that I accept the privilege from you to add something to the discussion. Previous to the war refractory material was manufactured in this country equal to anything imported from abroad, but many of the users in the metallurgical and other industries were prejudiced against the idea that material could be obtained for their purposes, and even when it was offered to them would not look at it, and if they did were not always willing to pay for it. This was perhaps not to be wondered at, because it seems that the bulk of manufacturers in the refractory industries conducted their business on a rule-of-thumb principle, and as Dr. Searle remarked, "refractory materials in this country were chiefly made by men whose knowledge of either physics, chemistry, or mechanics was almost negligible," and I may add the position is still the same to-day in many large concerns, however much may be said to the contrary.

To judge from some of the remarks made at the meeting, one would infer that the firebrick industry, as a whole, would by the introduction of scientific principles into the manufacture of the material be able to satisfy all requirements.

Where two firms are working the same seam of clay, naturally, other things being equal, the one which selects its raw material and puts itself in the place of the user turned manufacturer should command a higher standing than the less careful competitor. It has to be remembered, however, that the same quality cannot be made by all even if the desire existed, and this is an idea held by quite a number of those engaged in the manufacture of firebrick. Each has to depend on his particular deposit of clay; the geological position occupied and the origin of the formation of it affects to a great extent the manufactured article.

The failure of much material is very often due to the fact that it is made from a face of clay which contains many different qualities interwoven through the whole, and the rejection of one piece would mean the rejection of it all. Where this is the state of affairs technical knowledge is not of much use, and is usually put aside if the works have to go on at all. It seems a strong statement to make, but it is not made without a foundation established on facts.

As regards Major Bywater's contribution to the discussion, it is a very exhaustive one, and covers so much ground that both from a theoretical and practical standpoint exception could be taken to a great many of the views expressed. He only tells half a truth, I think, when he says that German

retorts worked in this country had a life of more than double the period of the 700 to 800 days of the British-made retorts. Many years previous to the issue of the standard specifications for refractory materials by the Institution of Gas Engineers I saw retorts made in Scotland which had a life of 2,400 days and an average never less than 1,200 days. I mention this to prove what I stated in the earlier part of my remarks, that refractory material was made in this country equal to that of the continental makers.

Major Bywater also laid great stress on the rational analysis of clay as an important factor for those investigating the value of clays. From my experience it is of very little value, as the method cannot be employed with accuracy. The clay substance cannot always be broken up with sulphuric acid. $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ is practically insoluble in this acid, and often with kaolite and halloysite very unreliable results are obtained compared with the accuracy of the ultimate analysis, and the corresponding more reliable calculated rational analysis. Dr. Mellor in an article on the "Rational Analysis of Clays" * sums up a very good case in favour of the ultimate as against the rational analysis and shows differences which make the one incompatible with the other.

I am quite aware, of course, that chemical analysis as used by a manufacturer to recommend his goods is to those who know something of the subject of little value, but it is of great value to the manufacturer in controlling his mixtures. The consumer is pretty much in the hands of the maker, as an analysis of a brick does not tell him much.

Major Bywater shows an analysis of a clay of medium quality, and I infer he thinks there is nothing to indicate why it should not make a satisfactory firebrick. As the analysis stands it shows a large excess of free silica and oxide of calcium, and it would be much more inferior if the analysis showed it was not of a uniform composition. A piece of this clay might be made up of different veins, and taking the figure given for the percentage of lime it is quite possible 20 per cent. of the clay could contain 8 per cent. of lime, and 80 per cent. contain 0.35 per cent., or made up in some other proportion giving an average of 1.88 per cent. lime. Usually an analysis is made on an average sample of the clay fine ground, which does not show all that could be known. It is best to be broken up into pea-sized pieces and an average calcined at, say, 2,500° F. The various portions can then be separated and an analysis made of each.

The following gives two analyses made in the ordinary way :—

Calcined Samples.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO.	MgO.	Alkalies.
A.	65.27	29.87	3.74	.34	.29	.49
B.	65.66	29.47	3.45	.33	.47	.62

An analysis of A was made on the pea-size pieces, and on calcination it was found that 60 per cent. was dark-red in colour, 20 per cent. steel-grey, 10 per cent. white, and the remaining 10 per cent. a dark-brown fused appearance. The analysis of each portion gave—

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO.	MgO.	Alkalies.
60 per cent. portion.	65.28	29.15	4.26	.42	.31	.58
20 " "	54.27	43.50	2.23	trace	trace	trace
10 " "	80.17	17.52	1.54	.27	.17	.32
10 " "	60.14	30.00	7.61	.62	.42	1.21

* *The British Clayworker*, September, 1908.

Sample B was calcined in a similar way and each small piece was similar in colour; analyses made of a large number of small pieces gave the same result as got in the first results made on the usual sampling. It was evident, then, that this clay was one of more uniform composition. These clays made into sample bricks were, after burning, in appearance much alike, and it can therefore be seen how different makes of firebrick similar in composition could give different results under similar working conditions. On the other hand, consumers, when there was no evidence for doing so, very frequently blamed the brick instead of their own carelessness—such as faulty design, use of inferior mortars in building, no effort in trying to eliminate outside influences which go to attack the brick, and other well-known reasons. The causes of the deterioration of refractory materials is too big a subject, however, for me to cover in a written discussion.

I was particularly interested in Sir Robert Hadfield's list showing the composition of various fire-clays, etc., and I would like to make a few remarks with reference to the analysis given for Glenboig. If it refers to the Glenboig Company's material, it is not an average composition, and if the reference applies to the district it is also a statement which is open to question, as the fire-clay worked by the different firms in the district varies greatly both in quality and appearance, and this variation can be attributed to geological disturbances. Ten or twelve miles north of Glenboig the geological position of the clay mined is over a hundred feet higher than that of Glenboig. The Glenboig position there is occupied by fakes and sandstone. As there is no common geological name for the seams or deposits of fire-clay, as in the case of coal, the name Glenboig then is not a geological term, but refers to the products of the Glenboig Company.

The average composition of Glenboig clay is of a uniform character and is on the calcined sample the following—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	CaO.	MgO.	Alkalies.
59'22	35'31	3'03	1'37	'30	'28	'49

Large deposits contain up to 42 per cent. Al₂O₃ with a very small percentage of fluxing agents, and in different parts of the field the physical qualities vary, giving plastic and non-plastic clays of similar composition, the combination of which as desired, along with the peculiar methods of manufacture, places the finished product in a unique position.

In a paper read by Professor Gregory, of Glasgow University, to the Royal Society of Edinburgh (1909-10), vol. xxx. part iv. (No. 18), on the Glenboig fire-clay, he remarks that the absence of roots from the Glenboig clay suggests that the clay had a different mode of origin from the English carboniferous underclays.

Reference is also made to the investigation of the clay substance in the Glenboig fire-clay carried out by Professor Fawsitt, of Sydney University, who states that the chemical composition of the clay substance is practically identical with kaolinite, though it contains more combined water, but when the water has been driven off from this mineral at 105°C. the remaining H₂O is in the same proportion as in kaolinite, and only a microscopical examination shows it to be amorphous and not crystalline.

The decomposition of this clay substance by boiling in hydrochloric acid suggests that it is halloysite rather than kaolinite, and as Professor Gregory further remarks that in his opinion the hydrous silicate of alumina in this Glenboig fire-clay was probably formed by the decomposition of feldspar by carbonic acid, and that the Glenboig fire-clay was of special economic interest, I mention this as evidence to prove that the "mysterious virtues and vices

with which particular clays are primarily endowed," to use Dr. Mellor's phrase, is, I think, worth some consideration.

Dr. Mellor's Paper on the "Texture of Firebricks" cannot be too well studied by both consumers and manufacturers alike. Texture is, however, a more difficult matter to control on a large scale than the reading of the paper might suggest, the chemical and physical properties of the raw material entering largely into the matter.

I have seen samples of firebricks of close texture which, when reburned at a temperature of $2,400^{\circ}\text{F.}$, had then a very low porosity, showing that this clay required to be underburned if the texture had to be close and still have a certain amount of pore space. Even using a large proportion of grog, the physical and chemical properties of the raw clay used as a binder will affect the brick as regards refractoriness, resistance to varying changes of temperature, and texture. As a rule, the highly aluminous clays are the most refractory, and when made into bricks of close texture, provided the clay is flint-like in appearance and non-plastic, still retain a large volume of pore space. Where the clay, however, is very plastic and has a high degree of refractoriness, it does not seem to resist sudden changes of temperature. This may be due to the larger proportion of fine dust formed in grinding the clay and sintering at a lower temperature than a hard non-plastic clay.

As is known, clays have no defined melting-point, the length of fusion interval regulating the value of a clay.

These foregoing remarks may explain why at times bricks close in texture resist sudden changes of temperature better than other coarse-grained qualities. In the near future, I hope, Dr. Mellor will be able to give more light on this part of the subject, and that the successful meeting on the discussion of refractory materials will be the prelude to many more.

Mr. Mackey (Dublin) (*communicated November 28, 1916*): I notice that in the discussion there was no allusion to the many deposits of refractory clays and other material deposits in Ireland, some of which are exceptionally good. There are on one estate 17 distinct deposits of clay within 6 ft. of the surface, spread over 1,200 acres, containing from 80 per cent. to 90 per cent. of silica, and from 5.50 per cent. to 95 per cent. of alumina. One of these deposits contains—

	Per cent.
Silica	90.80
Alumina and ferric oxide	5.20
Lime	0.35
Magnesia	0.11
Moisture (by difference)	3.54

This is a good refractory clay and very plastic. But perhaps the most valuable deposit is that which is situated on the promontory forming the north-west side of Portacloy Bay, co. Mayo, and worked by the China Clay, Felspar and Silica Company, Ltd., of Dublin. One remarkable feature is its thickness. The promontory shows an average thickness of 40 ft. facing the bay, and rises to 300 ft. at its other face, which faces Broad Haven. It is near this face that development work has been done, and tests have proved its great extent. Its outcrops on this side show a face 300 ft. thick, so that it is easy to test the quality at this depth. The overburden being on an average 11 ft., it is easily quarried. Tests have been made both for the production of silica and clays; among many, I might mention one made by Dr. J. W. Mellor, who found that the refractability of the washed clays was—

Cone 34-35 ($1,750$ – $1,770^{\circ}\text{C.}$; $3,182$ – $3,218^{\circ}\text{F.}$).

Residue after taking out clay from crude—

Cone 26 (1,580° C. ; 2,876° F.).

Crude without any treating—

Cone 30 (1,670° C. ; 3,038° F.).

As the crude (silicate of alumina, for this is what the deposit is) contains such a large quantity of free silica, this is easily separated, leaving combined silica and alumina in the proportions of 49 per cent. silica and 38.42 per cent. alumina, so that by mixing these two in the proper proportions, any grade of refractory body can be made. I might say that analysis shows only 0.31 per cent. titanic oxide, and 0.34 per cent. ferric oxide, which is admitted to be very low. The facilities for shipping are exceptionally good (providing you can get the ships), seeing that there are $5\frac{1}{2}$ fathoms of water at low tide right up against the cliff, from which the materials run down a chute into the hold of ships.

Both from the crude and that with the silica washed out, glass of all kinds has been made with splendid results, but owing to the prohibitive rates no shipments can be made at present.

I might add that it is estimated there are at least one hundred million tons practically in sight, so there is little occasion to go out of the United Kingdom for supplies.

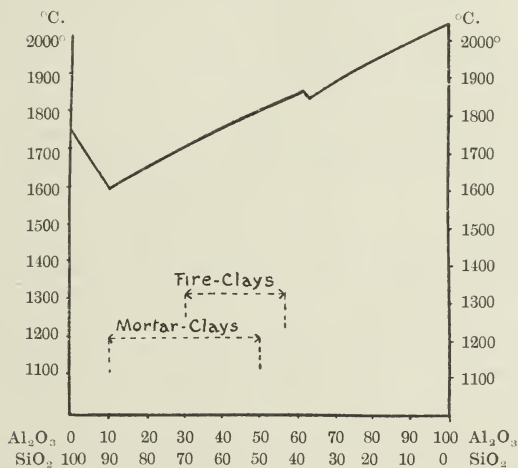
Professor J. W. Richards (Lehigh University) (*communication received December 2, 1916*): Not having the papers on refractory materials which were presented at the symposium, I cannot add to it any discussion of points advanced, but will confine my remarks to two topics which deserve more particular attention than is now being given to them, viz. refractory mortars for firebrick and silica brick and the properties of slag lining as a refractory material inside of water-jacketed furnaces.

Concerning the first item we know that when alumina is added to silica the melting-point decreases to a minimum at 10 or 12 per cent. alumina, thereafter increasing until the melting-point becomes considerably higher than that of silica for high alumina clays, such as kaolin, which when calcined is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

The function of a mortar is to adhere to the bricks which it unites strongly enough to make a gas-tight joint, but not to flux the bricks, for in the latter case it may form a fusible compound and run away entirely from between the bricks. Keeping this principle in mind, the best clay mortar for fire-clay bricks is one as high as possible in alumina consistent with having the necessary plastic properties. The lower in alumina it is, the more active will be its fluxing action upon the firebricks and the less desirable it becomes as a mortar. On the other hand, considering silica bricks, the most desirable mortar is that which is as low in alumina as possible, even to the most easily fusing mixture with 10 to 12 per cent. alumina. The reason for this is that a high alumina clay mortar acts as an active flux for the silica, forming large quantities of the most fusible mixture, and therefore may flux and slag the brickwork badly. It is no criterion of the suitability of a fire-clay mortar to be used with silica brick to say that its melting-point is as high as silica, because past 10 to 12 per cent. alumina the higher the melting-point the more alumina the clay contains, and the more actively it can flux silica brick to fusible slag. On this principle the fire-clay mortar for silica brick should be chosen with as low alumina content as is practicable for retaining the necessary plasticity. Many such

mortars used in the United States in coke-oven practice are mixtures of plastic clays with silica so as to total less than 10 per cent. alumina. When such mixtures are heated in contact with the silica brick, they can only adhere to or flux it slightly, because the instant that a 10 per cent. alumina mixture begins to attack silica the melting-point of the product rises towards that of the silica and the fluxing action is only superficial.

Finally, it should be noted that it is not at all sufficient to test by Seger cones the melting-point of brick and mortar separately in order to determine that the mortar is as refractory as the brick. This test may be entirely illusory, for the mortar, with an equal melting-point, may be a first-class fluxing agent for the bricks. The only rational test is to test the brick and mortar together, in intimate contact with each other, to determine the fluxing action and the melting-point of the *product*.



Regarding slag linings self-produced inside water-jacketed furnaces, such as is common in copper and lead smelting furnaces, there is great need for physicochemical determinations of the properties of these chilled slags. In practice their inside surface is constantly maintained at the melting-point, while their outside surface, next to the water jacket, is maintained approximately at 100° C. The thickness of the lining depends upon the intensity of the temperature inside the furnace, which is necessarily above the melting-point of the slag, and the higher above this melting-point it is, the thinner will be the automatically produced slag lining. But in all cases the slag lining, be it thick or thin, is always working between the limits of temperature already noted—that is, between its melting-point and 100° C. What is greatly needed, therefore, for metallurgical engineering calculations is the mean heat conductivity of some typical lead and copper slags between their melting-points and 100° C. These data would, for a given thickness of slag lining, determine the amount of heat which is being carried through it. If combined with determinations of the thickness of said lining for different furnace temperatures above its melting-point, the data would enable us to predict the heat flow through such slag linings for various furnace temperatures. Such desiderata are highly desirable, but depend upon the physicochemical measurements described. Such measurements could be made in a well-equipped metallurgical laboratory, but could possibly be determined in actual furnace practice by measuring the amount of heat carried away by

the water jackets, the thickness of the slag lining, and the temperature of the furnace, in various cases.

I have here merely indicated a fruitful and desirable line of metallurgical research.

Professor J. W. Cobb (The University, Leeds) (*communicated December 12, 1916*): A considerable amount of research was already in hand on clay and clay-silica refractories, and the specifications of the Refractory Materials Committee of the Institution of Gas Engineers had undoubtedly tended to raise the standard of manufacture, but our steel and other high-temperature industries, especially those using electrical furnaces, demanded a much higher grade of material, and experimental work in the laboratory and the works was essential to open the way for its provision. The proper handling and use of magnesia, for example, as a refractory was very little understood. A brick made from the purer Grecian (or Indian) magnesite was not at all the same thing as one made from Styrian material, which was impure from oxide of iron and other substances; the first was extremely infusible, and so well adapted for very high-temperature furnaces, particularly if for chemical reasons iron must not get into the charge, but it was not so tough or dense as the Styrian product, and for that reason not so highly regarded by many steel-makers, who normally imported Styrian bricks in some quantity; it was to be remembered that considerable quantities of impurities might be present in magnesia without inducing fusibility at steel furnace temperatures, although a certain degree of softness under load seemed to be characteristic of all magnesia bricks. In America experiments had been made to arrive at the properties of the Styrian magnesite by experimental additions to the Grecian and other purer material, but were reported as unsuccessful. He believed that problem to be in no way insoluble, and indeed steps to a complete solution had already been made in this country, but much work was called for to bring the properties of magnesia under control. Silica might be described as an intermediate refractory, and the making of the silica bricks was an established industry in this country, but how much was understood of the scientific principles involved? One thing was quite clear, and that was the inability of chemical analysis to determine whether a silica rock would or would not make a satisfactory silica brick, and presumably the officials of the Geological Survey concerned were taking that into account. Petrographic examination on the lines suggested by Professor Fearnside would probably be of service in that connection, and results of such work had been published by Endell.

Alumina and highly basic alumina-silica mixtures were very infusible and chemically resistant, but there were at least two considerable obstacles in the way of using them on any large scale. In the first place alumina (unlike silica) did not occur naturally in any high degree of purity. Bauxite was the most available form, and it usually contained considerable quantities of oxide of iron and silica, indeed some samples were not more infusible than ordinary fire-clay. The other great difficulty with alumina was the difficulty of completing its shrinkage before sending it out for use as a brick or block; the bauxite brick was often useless for this reason. The liability of alumina to reduction at high temperatures was also to be noted. As regards clay and clay-silica bricks, Dr. Mellor had issued a reminder of the importance of texture; it was impossible to lay down any valid general law that a fine-grained or coarse-grained brick was the better without reference to its use, because different conditions had to be satisfied, but it was perhaps safe to say that for a typical siliceous firebrick consisting essentially of a clay binder and silica grains the most general conditions of use would be met by making

the binder as fine and close-grained as possible, and the grains fairly large. It could at any rate be clearly established by direct experiment that the stiffening effect of a silica addition was lost if the material was very fine. This resulted from chemical and solvent action on the large exposed surface of fine silica and not from any intrinsic lack of stiffening power inherent in fine material, as has been clearly shown by experiments in which chemical action was excluded.*

He associated himself with Dr. Mellor in not regarding as reprehensible the addition of silica to fire-clay as a means of correcting after-shrinkage in use.

One pressing need of the carbonizing industry in some parts of the country was to arrive at the lining for coke ovens and retorts which would be most effective in resisting the action of salt in the coal charge, and texture was one of the most important factors concerned, as affecting both intrinsic fusibility and liability to penetration by alkaline vapour. The physical properties of refractories capable of numerical expression, such as thermal conductivity and coefficients of thermal expansion, at different temperatures, and particularly high temperatures, would require long and careful inquiry before they could be completely tabulated. He admitted the theoretical basis of Mr. Griffiths' criticism on the application of the guard-ring principle as made by Dougill, Hodsman, and himself in their apparatus for the determination of thermal conductivity, but was not convinced that the use of a thermal insulator ring would not introduce a more considerable error than the one it eliminated, which must be extremely small.

There was ample room for research on refractory materials, and since, as had been pointed out, the art was sometimes ahead of the science, the linking up of laboratory work with the large scale practice of both manufacturers and users of refractories was more than desirable; it was the primary essential. At any rate they were proceeding on that assumption at the University of Leeds. He had himself often realized at a certain stage in an investigation how impossible it would have been to make any further progress without the opportunity for taking the next step on the manufacturing scale, and testing the results in works furnaces under observation. Such phenomena as the inter-penetration and combination of solid oxides, which were no doubt in Professor Turner's mind when referring in the discussion to his (Professor Cobb's) work,† were often too slow in manifestation for purely laboratory experiment, although theoretically and practically of fundamental importance.

The President : In concluding the proceedings this evening as Chairman, I have the right and privilege to sum up in one or two words. I am not going to take more than a few minutes. In the first place, I am sure we are all convinced that this is a subject which is of vital interest to the nation. How is that to be brought home to the nation? It seems to me there should be some co-ordination in this connection, and the various societies concerned ought to have brought before them the extremely important information which has come out in the various Papers and contributions to the discussion. There are many thousands of people in this

* *Gas World*, April 1, 1916.

† *Journal of the Society of Chemical Industry*, 1910, pp. 69, 335, etc.

country who will never know of this meeting, and yet all who have been present this evening have seen how valuable are the results to be obtained from the discussion. The other suggestion I would like to make is that this same set of Papers should be repeated locally in several districts. I do not know whether that commends itself to your judgment, but it seems to me that if these Papers were read in the North of England and Scotland, and also perhaps in Sheffield, much good would result. Perhaps some of those who are present this evening from those centres may think it over. A great deal of information has been given to-night which is well worth repetition elsewhere.

THE DETERIORATION OF REFRACTORY MATERIALS IN THE IRON AND STEEL INDUSTRIES.

The following Papers on "The Deterioration of Refractory Materials in the Iron and Steel Industries," and "The Standardization of Refractory Materials used in the Iron and Steel Industries," by **Professor H. B. Cronshaw, B.A., Ph.D., A.R.S.M.** (University College, Galway), were communicated to the Society after the meeting.

The following discussion is an outcome of an attempt made to trace the agents concerned in the destruction of the refractory portions of furnaces used in the iron and steel industries, and the manner in which this destruction takes place, by actual examination of the furnaces themselves, and by the application of petrographical methods involving the use of the high-power microscope. It is intended here to record only the main outlines of the work. For additional details concerning refractory materials used in the iron and steel industries, reference may be made to two papers by the author, included in the bibliography given at the end of the present one.

In view of the recent awakening of interest in all that concerns the manufacture and utilization of refractory materials, it is almost superfluous to direct attention once again to the vital importance of formulating standard specifications. Nor is it necessary to point out the vast field of research which still remains to be covered, and the great possibilities which underlie the application of petrographical methods and of the principles of mineralogy, with especial reference to recent work on the behaviour of minerals and mixtures of minerals at high temperatures. Although this applies generally to all metallurgical industries in which refractory materials are made use of, it assumes a special importance in the case of the iron and steel industries. This is not surprising when one considers the excessive demands made upon the refractory linings of iron- and steel-making furnaces of every description. Working conditions are becoming more severe and efforts are continually being made to economize in working expenses, and hence arises the necessity for a corresponding advance in the manufacture of fire-bricks. The extent to which this has been carried out can best be judged by the consumer himself. Whatever the opinion may be, there can be no doubt that, as matters stand at present, the refractory linings in all types of iron and steel furnaces undergo far too rapid destruction, especially in particular parts of certain furnaces. The effects of this on the total working costs are sufficiently obvious, so that this consideration alone would justify any attempted investigation into the reasons for this excessive rate of deterioration.

It is clear that, whatever the destructive agents may be, they must vary in nature and intensity according to the type of furnace and the particular part of it under consideration. In other words, each part of every refractory lining is exposed to attacks from certain definite destructive agents of a chemical and physical nature, so that the wear and tear is by no means uniform and entirely due to one cause alone. Thus, for the bricks to

efficiently withstand these influences, they must be endowed with special chemical and physical qualities, and before these required qualities can be specified by the consumer for any part of his furnace-lining he must be fully acquainted with the adverse conditions which prevail at that point. And so it is for each part of every type of furnace; the first step towards supplying a lining is to ascertain the destructive forces at work in every part of it, as well as the rate and manner in which the destruction takes place.

OPEN-HEARTH FURNACES.

Construction.—The nature and arrangement of the bricks used in constructing the lining of an open-hearth furnace vary, of course, to some extent according to local practice. The variation is, however, not very great, and examples may be cited as illustrative of general practice.

In the case of a typical furnace of the acid type, silica bricks are used for the roof, sides, and blocks. The hearth consists of numerous layers of fritted sand, banked up to the doors and resting upon a stepped arrangement of silica bricks. For the main portion of the blocks an inferior type of brick is often employed. In one particular instance the roof measured 9 in. in thickness, the sides 18 in., whilst the bottom comprised 6 in. of silica bricks and 15 in. of fritted sand.

In modern basic furnaces magnesia bricks are employed in the construction of the bottom, ends, gas-ports, the back wall to within four courses of the roof, and for the front wall up to the springing of the arches. The roof, together with portions of the walls and blocks, are built of silica bricks, whilst the doors are faced with ganister bricks on the inside and ordinary firebricks on the outside. The hearth consists of a mixture of dolomite and tar. For further protection most modern furnaces are furnished with a system of water-cooled pipes passing round the doors, the ports, and the junction between the movable blocks and body of the furnace. In ordinary cases the sides measure 2 ft. in thickness, the roof 18 in. at the centre and 12 in. near the ends, the dolomite hearth 12 in., and the magnesia bottom 2 ft. Such an arrangement with these measurements would apply, for instance, to a 150-ton Talbot furnace of recent design.

Destruction.—Furnaces of the acid type described above were stopped each Saturday at noon, so that any necessary repairs to the lining could be carried out during the afternoon. This discontinuance of operations, and the cooling down of the furnace, together with the employment of skilled labour working under very adverse conditions, is an extremely serious matter and an obvious source of considerable expense and loss of time. Firing was not resumed until 3 o'clock on Sunday morning, and at about 7 o'clock the furnaces received their first charge of cold pig iron. Furnaces of this type, without slag-pockets, usually survive some 19 weeks, or 144 heats, before being stopped for serious repairs, or partial rebuilding, which may consist in the erection of a new roof and sides. With slag-pockets, however, this brief term may be lengthened to some 22 weeks, or about 198 heats.

In the case of modern basic furnaces, repairs are carried out at the end of every heat by the aid of chromite mortar, especially near the doors, which is of course an expensive operation. Furthermore, on Saturday afternoon the gas has to be cut off, the blocks drawn back, and all faulty places repaired under the same trying conditions mentioned above. For the blocks ganister mortar is used, near the water-pipes and in the body of the furnace chromite is employed, while crushed dolomite is thrown upon the hearth. At the end

of about 18 weeks the roof may be reduced from 12 or 18 in. to some 2 or 3 in. in thickness, and this, together with the front wall, usually requires rebuilding. The back wall is, however, not so easily destroyed, for at the end of this period it may vary from about 9 in. in thickness at the upper parts to about 18 in. where it meets the hearth, and can consequently be repaired without the necessity of total reconstruction.

Roof.—If the interior of a furnace is examined, when cooled down for repairs, the inner surface of the roof will be found irregularly eroded into hollows and grooves. Fissures run in various directions, and holes occur where portions of the bricks have fallen away. In certain places the surface presents an embossed appearance, with the depressions coinciding with the joints between the bricks. Everywhere the exposed surfaces are glazed and darkened in colour, so that the most casual observation points to important changes in texture and composition. The extent of this erosion is by no means uniform over the whole roof. In the central portions, above the middle door, a greater general depression occurs than elsewhere. Towards either end of the furnace the furrows frequently show a definite arrangement, spreading out fanwise from the air-ports. In the case of furnaces having air-ports at the upper corners of the end walls, the roof is traversed at either extremity by two longitudinal hollows separated by an intervening ridge. This curious arrangement of grooves evidently points to either the influence of abrasion or to fusion by contact with the flames along certain lines determined by the inflowing currents. No definite evidence is at hand by which a choice can be made between these two factors. Very probably both take a share in the work, as both are certainly active in these regions. Particles of dust which have accumulated upon the upper surfaces of the regenerator chequer-bricks are swept into the body of the furnace by the incoming air and producer-gas. Impelled upon the roof they must, in the course of time, effect abrasion much in the same manner as the familiar sand-blast. The intensity of this bombardment will fall off as the particles penetrate farther into the interior of the furnace, on account of decreasing velocity and their probable fusion. That the "cutting action" of the flames is a matter of practical importance is shown by the steps taken to prevent, as far as possible, any actual contact with the roof. In the central portions of the roof the rate of erosion reaches a maximum. Here the bricks, which frequently crack and break away, experience rapid changes in temperature, due to the opening and closing of the doors and the introduction of cold charges. This results in differential movements between both the constituent particles of the bricks and the bricks themselves, so that the strains set up are occasionally relieved by fissuring and general disintegration. Thus, although abrasion and differential movements certainly do take some share in the general deterioration of the brickwork, their importance as self-contained denuding agents in normal cases must not be overestimated. Thus in one particular instance a trial was made with "non-expansible" bricks in the roof of a furnace with unsatisfactory results; erosion proceeded much the same way as before. Rather must these physical agents be looked upon as assisting another and much more potent factor, that of fluxation.

The inner surface of the roof in its fused and sticky condition retains all dust particles swept against it. This dust, consisting chiefly of ferric oxide and lime, is derived from regenerators, producers, material charged into the furnace, and the occasional violent spurting of the bath of molten slag and iron. In addition there is the action of certain compounds in a volatilized condition. It is important to note that the central portions of the roof, where denudation is greatest, are most exposed to the lime and ferric oxide of the

charges. Thus all basic dust and volatilized products which are brought into contact with the silicious roof combine to aid in a general process of fluxation. Whenever cracks are present, whether large or microscopic, the fluxing action is somewhat assisted owing to the penetration of dust, vapours, and small quantities of slag into the interiors of the bricks. Evidence of this is to be found in the frequent embossed appearance of portions of the roof, brought about by more rapid erosion along lines of the joints. In the absence of cracks the slag resulting from this surface fluxation of the roof seems unable to penetrate of its own accord into the interior of the bricks, which means that porosity and permeability are of less moment than one might at first sight suppose. As soon as a certain quantity of slag has accumulated it is doubtless swept away by the inrush of the gases. That this failure of the slag to permeate through the body of the bricks is actually the case can be seen by examination of a brick taken from the roof of a furnace after completing its usual term of life.

A typical example of such a brick is represented in Fig. 1, which is a photograph of a high-class silica brick taken from the central portion of the roof of a 150-ton Talbot furnace after a period of 18 weeks. As regards texture, colour, and general appearance, four zones, A, B, C, and D, are plainly distinguishable, and the end, A, was the one exposed at the inner surface of the roof. In the photograph the black edge represents the fused and slaggy portion, which on its inner surface is clearly seen to be sharply marked off from the interior. At A is a light-grey, porous, and somewhat friable band about 1 in. in width, and this is followed by a black zone, about 2 in. in width, containing a few fragments of white grog, but very similar in texture to A. This passes more or less abruptly into the section C, which is very dark olive-green in colour, and crowded with angular pieces of grog. Lastly there is a narrow strip of comparatively unaltered material, represented by the band D.

Fragments were removed from each of these four zones and made into thin transparent sections by the usual petrographical methods for detailed examination under the microscope. A section cut from an unused brick of the same kind shows angular fragments of grog embedded in a brownish coloured groundmass; see Fig. 2. Under a high power the grog resolves itself into a mosaic of small, subangular particles of quartz, closely packed together and enclosing numbers of minute bubbles. They are fairly uniform in size, and are separated from one another by films of what appears to be chiefly oxide of iron. On the other hand, the groundmass consists of generally larger individuals of quartz, varying considerably in size, and embedded in an unresolvable brownish matrix of oxide of iron and lime. In the partly altered portion, D, at the upper end of the used brick, the grog, apart from the formation of small amounts of glass between the fragments of quartz, remains in a practically unaltered condition. The groundmass, however, is completely changed. The irregular fragments of quartz have disappeared, and in their place are minute well-shaped crystals, apparently of the same mineral, embedded in a brownish glass. In C the grog is still unaffected, but the crystals of the groundmass have become somewhat larger, more transparent, and more sharply outlined. In B (see Fig. 3), the material of the grog has suddenly become transformed into a brown, glassy matrix crowded with extremely minute crystals of quartz. Furthermore, the crystals in the groundmass have grown considerably into clear, well-formed individuals, which show undulating extinction and give anomalous interference colours, and the brown, glassy matrix has developed skeleton crystals of microscopic size. Within the last and most altered zone, A

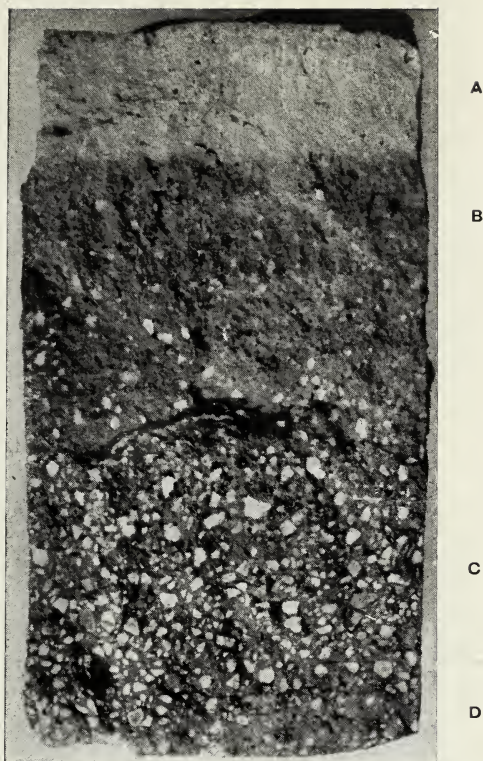


FIG. 1.—Silica brick from the roof of a 150-ton Talbot furnace after 18 weeks' use. Reduced to about one-third natural size.

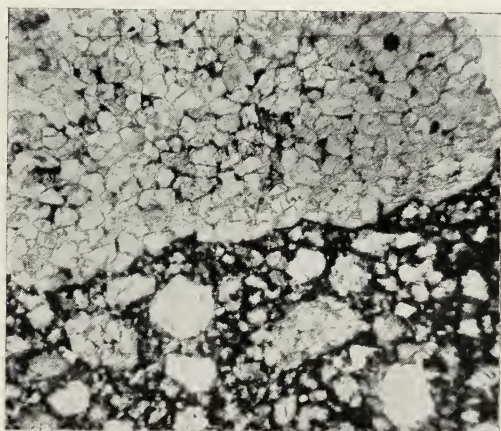


FIG. 2.—Unused silica brick for roof of an open-hearth furnace. Shows part of a grog fragment embedded in the darker groundmass.

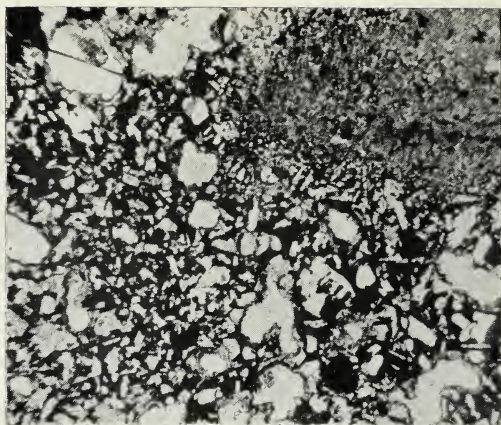


FIG. 3.—Section from the centre of the same brick after use. The fine-grained patch represents an altered grog fragment.

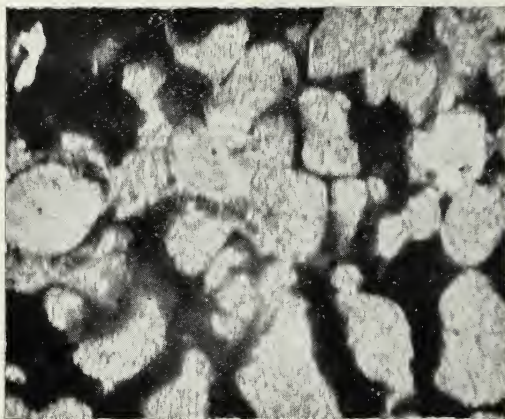


FIG. 4.—A section of the same brick taken near the exposed surface, showing aggregates of overlapping scales of tridymite.

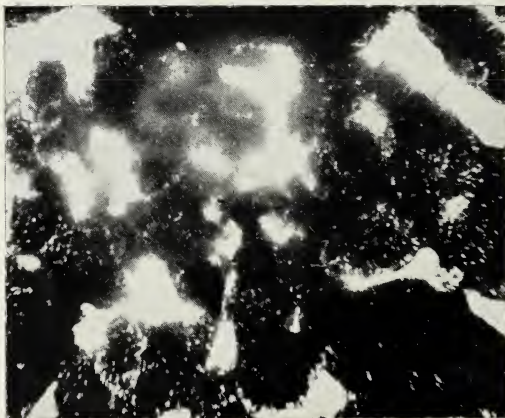


FIG. 5.—Section of an unused magnesia brick, illustrating the relation between pore-spaces and groundmass.



FIG. 6.—Section of fused surface of a silica brick taken from the block of an open-hearth furnace. Shows acicular crystals embedded in a glassy groundmass. The two light patches are remnants of grog.

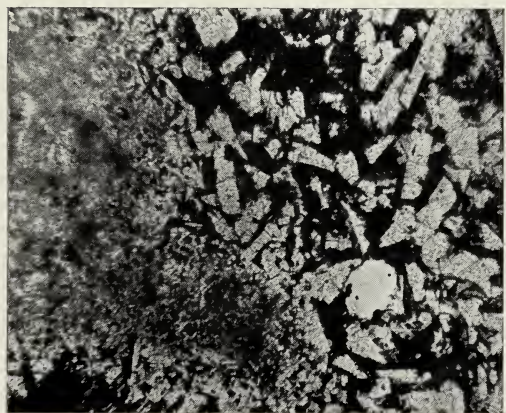


FIG. 7.—Section from centre of brick taken from the block of an open-hearth furnace. The fine-grained patch represents a grog fragment.

(see Fig. 4), a further change has resulted in the conversion of crystals in both grog and groundmass into a mosaic of overlapping and roughly hexagonal scales, arranged like tiles on a roof, and having a very low birefringence and index of refraction. These scales appear to represent the polymorphous modification of quartz, viz. tridymite. In spite of this change, the original crystals have retained their partly hexagonal outlines, although in substance completely replaced by the tridymite. Between these clear, scaly aggregates is a yellow-brown glass crowded with brownish, coloured skeleton crystals. As regards the outermost and fused margin, which contains very many skeleton crystals of magnetite, chemical analysis showed an increase in content of oxide of iron and lime when compared with unaltered portions.

Sides.—With silica brick walls destruction proceeds very much in the same way as in the roof. The action of slag is, however, somewhat different, in that it creeps down the walls and tends to accumulate near the bottom. As a result the slag is given a better opportunity of penetrating into the brickwork by means of cracks and fissures.

In cases where the walls are constructed of magnesia bricks, chemical activity is much reduced. Here the chief cause of destruction seems to arise from shrinkage of the exposed ends of the bricks, thus opening up fissures along the joints. This shrinkage in magnesia bricks is often considerable, as can be seen by examination of any furnace. Generally there is slagging, and the only other obvious changes are to be found in decrease of porosity and a darkening in colour. Fig. 5 represents a photomicrograph of an unused magnesia brick and illustrates their extremely porous nature.

Port-blocks.—Although here the temperatures are lower—about $1,100^{\circ}$ C.—than in the actual body of the furnace, yet the exposed brickwork comes more directly under the fluxing influence of the dust. Examination of the passages when the blocks are drawn back, shows clearly that there must be a constant creep of slag down the walls. Bricks taken from the blocks frequently show the banding observed in roof-bricks, though not so clearly marked.

A micro-section of the fused surface of a silica brick (see Fig. 6), taken from the air-flue in the block of a Talbot furnace, shows numerous crystals with a low birefringence and straight extinction, embedded in a greenish-yellow glass. Where free to develop they have formed needle-shaped individuals without definite terminations, but where more crowded together they are stumpy. Basal cleavage-cracks are well developed.

Another section (see Fig. 7) of the centre of a silica brick taken from the block of a Siemens basic furnace shows the same general features as the last, except that the matrix is crowded with skeleton crystals of magnetite and the outlines of grog fragments are preserved. The interiors of the grog fragments are occupied by glass containing a few small remnants of the original quartz grains, thus representing the final stages of solution.

Conclusions.—Within the body of the furnace and along the sides of the passages through the blocks, the main cause of deterioration is apparently to be sought in the slagging effects of, firstly, the basic dust derived principally from the charges, but also to some extent from the regenerators and producers, and, secondly, the particles of slag shot up from the melt at times of violent ebullition and the vaporized compounds derived from various sources. There are other factors which come into play, helping these chemical processes to an extent depending on the particular part of the furnace under consideration. At the end portions of the roof excessively high temperatures, abrasive

action, and the sweeping away of any accumulated slag to expose fresh surfaces for fluxation, are the predominant physical influences at work. In the central parts of the roof, where rapid changes in temperature result from frequent opening and closing of the doors and the introduction of cold charges, differential movements and strains in the brickwork are relieved by fissuring and a falling away of large and small fragments. It is probable that fissuring alone is not important in absence of accumulated slag, but the breaking away of portions of the bricks will expose fresh surfaces for attack by chemical agencies. In this region, also, fluxation proceeds most rapidly on account of the repeated supply of basic dust from the charges.

In the case of silicious walls, the presence of fissures will facilitate the penetration of slag, and hence promote internal fluxation. When magnesia, chromite, and similar materials are employed, chemical activity is reduced and deterioration practically entirely results from shrinkage. At least this is so in the case of magnesia, which finds general use at the present day for parts of the walls.

Within the passages through the blocks the temperature is lower, but the dust, being confined within less space, is brought more intimately into contact with the exposed surfaces. Physical and chemical processes are both active, and a good deal of slag is formed. At the ports destruction proceeds more rapidly, mainly on account of the high temperatures which prevail there.

REGENERATORS.

Most regenerators are built on the same general plan, and practically all modern types are fitted with slag-pockets. For construction of the chequer-work ganister bricks are in common use.

The gas-chambers of regenerators attached to large Talbot furnaces last about 18 months before the chequer-work requires replacing. In the case of the air-chambers this period is reduced to some 12 months. During this time, however, the chambers are frequently opened up for general cleaning and removal of as many broken and fluxed bricks as possible. For instance, the regenerators attached to a certain 150-ton Talbot furnace had to be opened only 14½ weeks after the installation of new chequer-works. Even after this brief use, a considerable amount of destruction had taken place in a manner which is described below. In other cases, where basic Siemens furnaces with slag-pockets were in use, the gas-chambers were run for about two years and the air-chambers about one year before being rebuilt. On the other hand, both gas- and air-chambers attached to a set of acid Siemens furnaces, with slag-pockets, were only allowed some 40 weeks of active life. The installation of slag-pockets always has the effect of prolonging the lives of regenerators, and the quantity of slag which accumulates is remarkable, amounting, in the particular case of a small basic Siemens furnace, to a depth of about a foot per month. It is obvious, therefore, that the term of life which can be allotted to generators is a somewhat variable quantity. As all regenerators are built on the same general plan, it will largely depend on the type of furnace and the adopted practice.

Examination of the chequer-work in the case of the 150-ton Talbot furnace cited above showed that the upper surfaces of the bricks were thickly covered with chocolate-brown dust, which had fused at its contact with the bricks. This gave rise to a dark-coloured viscous slag, which had run over the sides of the bricks and collected in stalactites on their under surfaces. There was clear evidence of a dripping of this slag, from brick to

brick, through the whole chequer-work. At this early stage the bricks were not greatly altered; some were cracked and had to be removed, but the majority appeared to be fairly sound. On comparing the effects in air- and gas-regenerators, it was evident that in the former there was a greater amount of slag, and here, too, the chequer-bricks showed more obvious signs of general destruction. The central portions of the bricks were yellowish in colour, whilst the marginal portions were bleached, but apart from surface fusion the general texture remained much the same as originally. Within the gas-chamber there appeared to be quite as much dust, but fusion and slag formation had gone on to a considerably less extent. The colour of the fractured surfaces of the chequer-bricks was also different, being grey instead of yellow. In the case of regenerators which have been in use for longer periods than this, the effects of fluxation are, of course, much more striking. A particular instance in which the air-chambers had been in operation about a year, and the gas-chambers had been allowed to run on for the space of two years, will serve to illustrate this point, and the furnace to which they were attached was a small type of basic Siemens furnace, provided with slag-pockets. The chequer-bricks were very considerably reduced in size—in many cases to less than half their original dimensions. They were black in colour, and penetrated by numerous holes and fissures, and were fused practically entirely throughout. Generally their upper surfaces were somewhat depressed, whilst the under surfaces had assumed a convex form.

Analysis of the dust which collects upon the chequer-bricks shows that it principally consists of ferric oxide and lime, with a certain amount of silica and magnesia. The following is an analysis of chequer-dust taken after 14½ weeks from the gas-chamber of a large Talbot furnace:—

								Per cent.
SiO ₂	12·70
Al ₂ O ₃ }	60·70
Fe ₂ O ₃ }								
CaO...	26·30
MgO	2·19
								101·89

From this and other considerations there is no doubt but that the oxide of iron and the lime are derived from the charges, whilst the magnesia comes from the dolomite thrown upon the hearth when undergoing repairs. The main portion of the silica and alumina is doubtless derived from the fine particles of slag swept over from the furnace roof, from the surface of the melt during violent ebullition, and from the ash brought in by the producer-gases. When a basic dust such as this settles upon the white-hot surfaces of silicious bricks, the results are quite obvious. The destructive effects are further accentuated by the accumulation of the slag upon the upper surfaces of the bricks, so that the existence either of cracks or of a high degree of permeability becomes an important factor—much more so than in the case of the furnace-lining.

Micro-sections prepared from the surface of a brick taken from the chequer-work of an air-chamber after a period of one year showed fragments of grog, with their quartz grains still preserved, embedded in a brownish glassy groundmass crowded with extremely minute lath-shaped crystals having a very low index of refraction and birefringence. Both are

lower than those for quartz appearing in the same section. In the case of a slice taken from the interior of a chequer-brick belonging to the gas-chamber, and after a period of two years' use, the same features as described above were presented, except that all traces of original quartz had disappeared.

Thus the deterioration of the regenerator bricks, is mainly of a chemical nature, and is to be attributed to the fluxing influence of basic dust, derived principally from the charges, but partly also from the producers and from slag carried over from the body of the furnace. Furthermore, this fluxing action is very materially assisted by the development of cracks within the bricks, and by the existence of any degree of permeability, owing to the fact that the slag is allowed to collect upon the upper surfaces of these bricks. The slagging is also accumulative in the sense that any overflow drips from brick to brick through the chequer-work. The difference in terms of life between gas- and air-chambers is a further indication of the important part played by chemical influences.

BLAST-FURNACES.

Above the bosh the lining is generally constructed of common firebricks, but within the bosh and hearth the same bricks are faced on the inside with high-grade firebricks. The term of life allotted to a blast-furnace lining varies considerably in different cases, depending to a very large extent on the particular practice adopted.

Deterioration of the brickwork proceeds in a variety of ways, and the influences vary in nature and intensity from point to point within the furnace. A very good idea of the general results can be gained from the consideration of a lining which, at the time of examination, was being replaced after some thirty-eight years' continuous service. Within that portion of the shaft between the top of the bosh and a point some 13 ft. below the top of the furnace, a thickness of about $2\frac{1}{4}$ ft. of brickwork had been removed by denuding influences. Within the bosh, however, the lining retained its original thickness, but was to a large extent replaced by carbonaceous matter, to form the black, porous, and somewhat friable "scar." This "scar" first appeared at a depth of about 28 ft., and increased in thickness when followed into the bosh. Traced into the walls, it gradually died out and gave place to the outer layers of brickwork, which, apart from fissuring and cracking, showed remarkably little evidence of alteration. There were no signs of fluxation or fusion. Deposited within the fissures, pores, and crevices between the various layers of brickwork were numerous small yellow hexagonal crystals of zincite, containing 99 per cent. of zinc oxide and 1 per cent. of lead oxide. In addition to these, other minerals occurred, both within the outer layers of "scar" and within the unaltered brickwork. Such, for example, were deposits of soda, potash, and chlorides of sodium and ammonium. The zincite is said to have first made its appearance, in abundance, at a depth of about 35 ft. below the top of the furnace, whilst at various points below a depth of 20 ft. a good deal of white, powdery, and deliquescent zinc chloride was found by those engaged in pulling down the lining.

From these and other considerations one can form an opinion as to the extent to which the several destructive processes are operative in the different sections of the furnace. Near the top of the furnace, where temperatures and chemical activity are lowest, the brickwork comes under the abrasive influence of material charged into the furnace. That these effects of impact

and abrasion are considerable can be gathered from the frequent use of cast-iron "wearing-rings."

Within the shaft the deterioration reaches a maximum, and forms the chief reason for the blowing-out of the majority of blast-furnaces. As pointed out above, the inner and more exposed parts of the shaft-brickwork become progressively replaced by the carbonaceous "scar," and the process of replacement can be clearly followed by the study of micro-sections cut from unused bricks and various parts of the "scar" and partially modified bricks. Sections of unused bricks show that the finely divided groundmass of quartz grains and argillaceous material is crowded with minute particles of iron oxide. To some extent they are also enclosed in the quartz grains of the grog. Approaching the "scar" the bricks assume a peculiar bluish-black colour, which deepens along with a change in texture, until within the "scar" itself all traces of the original texture and form of the bricks have disappeared, leaving a black, scoriaceous material, in which the small cavities are filled and lined with graphite. Micro-sections of the partly altered and bluish-black bricks show fragments of quartz enclosed in a groundmass crowded with carbonaceous dust, but within the inner portions of the "scar" itself all traces of the original quartz have disappeared; there is no argillaceous matter or oxide of iron, but instead dense aggregates of finely divided carbon contained in a matrix of overlapping, hexagonal scales of tridymite. Graphite can be seen filling or lining the numerous small cavities. The "scar" is relatively friable, and thus easily succumbs to abrasive action and local scaffolding. On the other hand, it protects the external layers of unaltered brickwork from the direct influence of heat and fluxes, but, doing so, permits the deposition of those various types of minerals mentioned above, which, besides assisting in the general process of crumbling and fissuring, constitute a source of danger in the event of local overheating. On such occasions the temperature may rise high enough to promote interaction between the bricks and deposited compounds with, for instance, the formation of alkaline silicates, so that fluxation would result and possibly give rise to local heat-spots. In one sense therefore the "scar" is protective, and in another destructive. It protects the relatively unaltered brickwork from the high temperatures and chemical activity of the charges, but at the same time it gives rise to conditions which favour the deposition of volatile compounds, locally capable of bringing about serious destruction of the lining, and moreover constitutes in itself a source of progressive and effective destruction, arising from its relatively friable nature.

Within the bosh high temperatures and chemical activity predominate, whilst the influence of abrasion and scaffolding hardly makes itself felt. In this region the formation of "scar" takes place to a greater extent than elsewhere, but in absence of serious abrasive action its influence is protective rather than destructive.

Chemical activity at high temperatures becomes an important feature in the hearth, and here, below the level of the melt, the presence of any fissures would lead to internal fluxation and a tendency to disruption of the brickwork on penetration of the molten iron or slag. By using cooling devices chemical activity is diminished, and probably a layer of solid or partly solidified slag or iron is formed against the lining.

CUPOLAS.

Although cupolas vary considerably in constructional details and actual working conditions, yet as regards general considerations dealing with deterioration of the linings, very much the same features must be presented

by all types. For this reason attention may be confined to a single example as illustrating conditions which generally prevail.

In this particular furnace, which is one of modern design, the interior was lined throughout with "best" firebricks to the extent of about 9 in. in thickness in the hearth and some $4\frac{1}{2}$ in. in the shaft. The working period extended from 5 a.m. to 5 p.m., during which time tapping was carried on at frequent intervals. The probable temperature of the metal during tapping was somewhere in the neighbourhood of $1,200^{\circ}\text{C}$., whilst within the melting zone the temperature varied between, say, $1,400^{\circ}\text{C}$. and $1,800^{\circ}\text{C}$. The hearth and bosh required total relining every six to nine months, whilst the shaft survived two or three years. Fettleing with ganister mortar had to be carried out every day, and also during the week-ends.

In general it may be said that cupola linings come under very much the same set of chemical and physical influences as blast-furnace linings. With regard to this particular furnace, however, there are several additional features of some importance which might be noted here. Within the shaft a good deal of the wear and tear could be attributed to the striking of lumps of pig and scrap iron against the sides during charging operations. In the bosh "scars" of iron, formed by local cooling due to the incoming blast, may cling to the sides, so that their subsequent removal is attended by serious damage to the brickwork.

Within the hearth the same trouble arises by the clinging of the slag to the sides during tapping. Another source of danger lies in the creation of oxidizing conditions, due to the use of insufficient coke or too much blast, resulting in the formation of iron oxide, capable of immediately fluxing any silicious material at hand.

CONCLUSIONS.

It appears, therefore, that in the case of open-hearth furnaces and their regenerators the main cause of deterioration is to be found in the fluxing influence of basic dust and volatilized compounds derived from various sources, but chiefly from the charges. Theoretically speaking the most obvious way of overcoming these difficulties is either to prevent any dust entering the furnace from both producers and charges, or else to suppress the dust before it can come in contact with the brickwork, or a third way would be to so adjust the composition of the bricks as to be neutral towards the agents in question. The first of these presents many practical difficulties, although there are several ways in which it might be carried out. However, if the whole of the fine dust cannot be removed on a large scale, nor its formation prevented during charging, there is no reason why care should not be taken to keep its amount as low as possible, for even this is certain to be attended by favourable results. The second way applies more particularly to regenerators, and an arrangement has been devised for eliminating the dust before it reaches the chequer-work. The third suggestion opens up a wide field for investigation. It seems highly probable that future research will point out a way of utilizing our natural deposits of basic minerals and rocks for the purposes of brick-making, without having to depend upon costly material brought over from other countries. Among such deposits implied may be mentioned those of bauxite, serpentine, steatite, limestone, dolomite, and magnesian limestone, although their successful application at high temperatures involves many problems which can only be solved by systematic research in co-operation with industry.

In blast furnaces and cupolas chemical changes are involved in fluxation by actual contact with the semi-fused charges and the liquid slag, in the for-

mation of scar, and as a possible result of the crystallization of volatilized compounds. To resist these influences the composition and texture of the bricks must be adjusted accordingly. With respect to the former it is especially important to have bricks free from oxide of iron if the formation of scar is to be prevented.

In addition to these destructive forces, which act chemically, there are others whose action is mechanical or physical in nature, and which, varying from point to point in different furnaces, occasionally become of first importance. Such are abrasion, differential movements, and permeability. Acting alone and in moderation the effects produced would not be very pronounced unless assisted by fluxation. Abrasion is probably only of moment in the shafts of blast-furnaces and cupolas. In the first it is considerably assisted by the formation of friable "scar," and in the second by careless charging. Differential movements, besides leading to general disintegration, tend to open up cracks and joints for the entrance of corrosive slags and vapours. The first become more important when assisted by gravity, as in the roof of an open-hearth furnace; the second, in those places like the hearths of blast-furnaces, cupolas, and open-hearth furnaces, and in the case of regenerator chequer-works, where the bricks are directly exposed to liquid slag. The existence of any degree of permeability also assists fluxation in precisely the same way.

Furthermore, there are other factors having a more general application which are capable of being brought more directly under control of the steel manufacturer, viz. workmanship, regulation of the temperature during the first heat, and the careful adjustment of all tie-rods. The joints being lines of weakness, every care should be taken to make them as inconspicuous as possible, but in spite of every effort this is generally unattainable, because of the great variation in shape and size which exists amongst firebricks of every description. This variation is at the root of many evils, for besides rendering the brickwork more susceptible to destruction, it considerably increases the cost of erection, due to loss of time and wastage of bricks. Very often this irregularity is due to the friable nature of the bricks, as in the case of those rich in silica. During transit and handling they become rounded at the corners, and chipped and fractured often to a serious extent.

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THE STANDARDIZATION OF REFRACTORY MATERIALS USED IN THE IRON AND STEEL INDUSTRIES.

BY PROFESSOR H. B. CRONSHAW, B.A., PH.D., A.R.S.M.

In writing the following notes the main object has been to direct attention to the urgent need of standard specifications for the iron and steel industries, and at the same time to venture several suggestions with regard to what appear to be the most useful standardized tests for this purpose.

It is well known that the properties—chemical and physical—of refractory materials ultimately depend on mineral composition and texture, but that only certain of these properties play any important part in determining their degree of refractoriness—using the term in its broader sense as indicating the ability of a substance to resist all forms of destruction, and not fusion alone. However, in any statement of refractoriness the conditions under which the material is to be placed must also be included ; a given substance may be highly refractory under one set of conditions, but completely fail under another. Thus standard specifications for any particular industry must state to what furnaces and portions of furnaces the standardized tests apply, and before limits can be set forth under the various tests, the chemical and physical conditions prevailing in each part of every furnace typical of the industry must have received full investigation. As soon as this is accomplished, and the extent to which specified qualities are reproducible in firebricks is known, then, as working expenses and output are largely affected by the quality of the refractory material used, it is all-important that every means should be taken to see that these materials are as highly refractory as possible and that the refractoriness maintains a uniform standard, or at least is never allowed to fall below a certain standard ; in other words, the time will be ripe for framing tests standardized for materials to be used in every part of the several furnaces. Our knowledge of furnace conditions as they affect refractory linings is far from complete, yet certain investigations carried out by the author, and outlined in a separate Paper included in this volume, have raised various points which seemed worth considering in the event of a general agreement being arrived at as to the advisability of taking immediate steps to draw up the required specifications. The suggestions offered must, however, be looked upon as merely tentative and open to criticism, for the real object in setting them down here is to promote a lively interest in this highly important question, rather than to dogmatize on controversial matters.

Mineral Composition.—Seeing that refractory materials consist of aggregates of minerals in the form of oxides, silicates, and other compounds, it is important to be able to estimate their nature and relative amounts, especially as these determine the extent to which a material is acid, neutral, or basic under particular conditions. Strictly speaking, this can only be done by the combined assistance of chemical analyses and microscopical examination

of thin sections. The former, of course, gives qualitatively and quantitatively the composition of the sample in terms of oxides of the constituent elements, whilst the latter serves to identify and, to some extent, quantitatively to estimate, what is important, the actual constituent minerals present. An exact quantitative estimate of mineral constituents cannot be arrived at by application of microscopical methods alone; for this purpose computation from reliable chemical analyses must be called into account, and the microscope becomes merely supplementary and serves to check the results. Where exact and comprehensive information is required, chemical analyses are absolutely necessary, but in view of the labour and expense involved in their performance, it is questionable whether every case which arises calls for this exhaustive treatment. For ordinary purposes, where economy and expeditiousness are required, a microscopical examination would supply all the information required, whether the sample be raw material or finished product. It is unfortunate that this aspect of the question has escaped general recognition. Moreover, even in those cases which justifiably demand a chemical analysis, one or more thin sections of the sample ought always to be available. Their value for purposes of checking the computations and of supplying additional information cannot be overestimated. In special cases, as in the examination for free oxide of iron, or in following the mineralogical changes which take place within the refractory materials at various stages in the course of their manufacture and subsequent use, the microscope would prove of great service.

Texture.—The thin sections cut for the above-mentioned purposes would also serve to supply all necessary information on the question of texture; that is to say, the precise form, size, and manner of aggregation of the constituent particles. By this means also the internal structure of the individual grains can be made out—that is to say, whether much shattered, traversed by comparatively few cracks, or quite free from them. Information of this kind would prove of great value in enabling one to form an opinion of the changes likely to take place when a sample of raw material or firebrick is heated, and a still wider field of utility would be created if correlated with the results of such tests as are usually included in standard specifications. Furthermore, in the final stages of brickmaking samples could be withdrawn from time to time, and within a few minutes a thin section would be available for examination so as to enable one to follow the changes taking place, and this would be the first long step towards gaining complete control over the manufacturing processes. The same applies to the bricks after being built into the iron and steel furnaces; here again thin sections would serve to indicate the mineralogical and textural changes taking place.

Uniformity in Shape and Size.—Sufficient has been said in the Paper quoted above to indicate some of the ways in which want of uniformity in shape and size will adversely affect the refractoriness of linings. No brick ought to depart from certain standardized measurements by more than a certain amount.

Position Marks.—It is probable that a useful purpose would be served by insisting that bricks designed for each particular part of a furnace should be correspondingly stamped by the manufacturer, so as to avoid any possibility of confusion in ordering and laying, and to generally promote a more systematic state of affairs. This is meant to apply more particularly to bricks of unusual form, but it might be extended, if desirable, so as to have a general application.

Softening Point.—This should be determined under strictly specified con-

ditions—similar, for example, to those set forth in the Gas Engineers' specification for retort material.

Permeability.—It is suggested here that instead of measuring the porosity, as is usually done, an estimate of permeability be made instead. The reason for this is that porosity, as ordinarily determined, is not necessarily a measure of susceptibility to penetration. For instance, the actual size and number of the individual pore-spaces, as well as their total volume and the condition of the intervening material—that is to say, whether permeable or not—are important points having an influence on this susceptibility to penetration, which constitutes what is really important for practical purposes. Therefore some standardized test on the following lines might be carried out.

A certain sized cube of the refractory material is prepared and half immersed for a certain length of time in a bath of molten slag raised to a definite temperature. The slag must be of a certain standardized composition corresponding to the one typical for the particular furnace in which the brick is to be used. The extent of penetration is then estimated by comparison of the original porosity—as usually defined—of a cube of the same size with the porosity of the cube after immersion. The manner in which this penetration has been effected could then be observed on examination of thin sections under the microscope—that is to say, whether, for instance, the slag has gradually soaked into the test-piece or advanced along certain cracks. Such a test could be elaborated so as to reproduce average working conditions as closely as possible, and in this event would yield results of undoubted practical value.

Resistance to Temperature Changes.—So far this important property seems to have escaped standardization, whereby prescribed tests can be carried out on samples and the results referred to a definite unit. What is needed is some test which involves the raising of the test-piece to a certain temperature, followed by a rapid cooling to a lower temperature during a definite period of time by a stated means, and then an estimation of the altered condition of the test-piece by a suitable method, such as a determination of crushing-strength, which on comparison with the original value would give a substantial measure of the ability of the sample to resist sudden fluctuations in temperature. Here again micro-sections would afford valuable evidence, and in addition would suggest methods for rectifying any undue cracking or disintegration.

Dilatation.—This is offered as a provisional term to imply the percentage linear expansion experienced by the test-piece when raised to a certain elevated temperature as nearly approaching practical conditions as possible. The measurements are made first before heating, and then whilst exposed to the prescribed high temperature. At present there appears to be no well-known method of carrying this out at the temperatures experienced in industrial furnaces, in spite of its great importance from a practical point of view. However, possibly experiments now being carried out by the author to determine linear expansion in minerals and refractory materials at very high temperatures may yield substantial results.

Permanent Expansion and Contraction.—The term "permanent" is used here, not in any absolute sense, but merely as a means of identifying this as a test separate from the last named. The measurements are made at normal temperatures, and the details of procedure are fully explained in the Gas Engineers' specification. The test is especially important as estimating the amount of Mellor's "after-contraction or after-expansion" resulting from incomplete burning.

Hardness.—A determination of hardness would be required in the case of bricks intended for special purposes, such as the upper parts of the blast-furnace and cupola shafts, and is determined by an abrasion test.

Toughness.—The same applies to an estimation of the capacity to resist impact, and can conveniently be measured by the usual attrition test.

Crushing-strength.—Used in conjunction with other tests as described above, the determination of crushing-strength may be made to yield useful results.

THE COMMON REFRACTORY OXIDES.

Mr. Robert B. Sosman, of the Geophysical Laboratory, Washington, sent in the following Paper on "The Common Refractory Oxides" as his contribution to the symposium.

In discussing the common "refractory oxides," we will confine ourselves to the common rock-forming oxides : silica, alumina, magnesia, lime, and the oxides of iron. These taken together make up practically 90 per cent. by weight of the accessible outer shell of the earth, while soda, potash, and water make up most of the remaining 10 per cent.

In comparing the properties of the individual oxides and in discussing their important compounds and mixtures, I hope to bring out certain general principles that will serve to classify and correlate in our minds some of the facts which have already been discovered, and at the same time show where additional research is needed.

The Pure Oxides.

One property of the oxides which is of primary importance is the melting-point. The melting-points of the common oxides are listed in Table I.

TABLE I.

Melting-points of the Common Refractory Oxides.

Silica, SiO_2 (quartz)	Below $1,470^\circ$
" " (cristobalite)	$1,625^\circ$
Alumina, Al_2O_3	$2,050^\circ$
Magnesia, MgO	$2,800^\circ$
Lime, CaO	$2,570^\circ$
Ferric oxide, Fe_2O_3	Unknown
Ferrosoferric oxide, Fe_3O_4	$1,580^\circ$
Ferrous oxide, FeO	Unknown

*Silica.**—Two melting-points are given for silica. The explanation of these introduces the very interesting set of allotropic forms that silica exhibits. I have attempted to give a graphic statement of the relations of these forms in one of the diagrams of Fig. 2.

Silica possesses to an unusual degree the property of responding very slowly to changes of temperature as regards its melting-point and its transitions from one principal form to another. Each of these principal forms, on the other hand, has one or two inversion-points of its own, which respond very

* C. N. Fenner, *Am. Jour. Sci.*, 36 (1913), 331-84.

promptly to temperature change. The principal forms are *quartz*, *tridymite*, and *cristobalite*. Quartz has a reversible inversion at 575° , tridymite has inversions at 117 and 163° ; cristobalite is peculiar in having an inversion-point whose temperature varies from about 200 to 275° , depending upon the previous history of the crystal. By rapid heating, quartz can be melted before it has had time to transform into tridymite or cristobalite.

The atomic or molecular basis for these interesting relations remains to be worked out.

Alumina.*—Two allotropic forms of Al_2O_3 are known. The common form, known as α , is the same as the mineral corundum. It was the only form which appeared in the lime-alumina-silica investigation by Rankin and Wright. The magnesia-alumina-silica study (by Rankin and Merwin) brought out a second or β form. At first it was thought possible that it might be a compound corresponding to magnetite, with the formula Al_3O_4 , but a chemical analysis by H. S. Washington shows it to be pure Al_2O_3 . Its relation to the α form is not yet known.

Magnesia.—Only one crystalline form of MgO is known: it is the same as the mineral periclase. Magnesia has the highest melting-point of any of the oxides here described ($2,800^{\circ}$).

Lime.†—There is only one crystalline form of CaO known at high temperatures. It seems to possess an inversion-point, however, at about 420° , which is similar to the 575° reversible inversion-point of quartz. The exact location of this point will require further investigation.

Pure CaO is, however, obtainable in two forms.‡ The first, which is probably amorphous, results from the dissociation of calcium carbonate at low red temperatures. On heating for a considerable time at higher temperatures, it changes gradually into the cubic crystalline lime of refractive index 1.83 . The latter forms directly from silicate melts or from fused calcium nitrate, and is the stable form at high temperatures. The porous lime ought not, perhaps, to be called a distinct "form," as it is probably not such in the sense in which cristobalite is a "form" of silica.

The porous, probably amorphous, form of CaO is much more reactive than the crystalline. It unites readily with dry carbon dioxide or with water, whereas the crystalline CaO unites only slowly with these compounds. The fundamental reason for this difference is yet to be found.

Oxides of Iron.§—The oxides of iron offer a research problem quite different in character from that of the other oxides described above, by reason of the fact that their compositions and properties at high temperatures depend upon the pressure of oxygen in contact with them.

Ferric oxide, Fe_2O_3 , which occurs in nature as hematite, begins to dissociate, as the temperature rises, into oxygen and a solid solution containing ferrous iron; this may be considered as a solid solution of Fe_3O_4 in Fe_2O_3 . At a given temperature the initial dissociation pressure is high, but it drops rapidly as the percentage of FeO in the solid increases, passing through a range in which the pressure falls rather slowly with change of composition, and finally falling rapidly to the dissociation pressure of Fe_3O_4 , which is very low (less than 0.04 mm. of mercury, at $1,200^{\circ}$).

Fe_3O_4 , in turn, dissociates into oxygen and a mixture of oxides whose character has not yet been determined.

The properties of FeO are still practically unknown. The most of the

* Rankin and Merwin, *J. Am. Chem. Soc.*, **38** (1916), 568-88.

† Rankin and Wright, *Am. Jour. Sci.*, **39** (1915), 1-79.

‡ Sosman, Hostetter, and Merwin, *J. Wash. Acad. Sci.*, **5** (1915), 563-9.

§ Sosman and Hostetter, *J. Am. Chem. Soc.*, **38** (1916), 807-33, 1188-98.

recorded methods for preparing "ferrous oxide" yield only a mixture of metallic iron (or iron carbide) with an oxide whose composition falls between FeO and Fe_3O_4 .

Ferric oxide has an inversion-point at 678° , which is sharp and reversible, like the 575° inversion of quartz. This point is marked by an absorption of heat, as the temperature passes 678° , and also by a sudden drop in magnetic susceptibility. According to Honda there is a similar inversion at -40° .

Fe_3O_4 is said to have a similar magnetic inversion-point at about 530° , when it suddenly changes from a "ferromagnetic" to a "paramagnetic" condition. We have not yet investigated this inversion thermally.

The relations of these inversions to one another, and to the similar inversions in pure iron and in steel, offer an interesting field for future study.

Two- and Three-Component Systems of the Oxides.

In order to give a comprehensive and concise view of the relationships of the compounds and mixtures which can be made up from any two or three of the refractory oxides, I have compiled the accompanying diagrams (Figs. 1 and 2). The facts are expressed in the form of phase-rule diagrams of all the possible two- and three-component systems which can be made up from the six oxides SiO_2 , Al_2O_3 , MgO , CaO , Fe_2O_3 , and FeO . From these six oxides there can be made 15 two-component systems and 20 three-component systems, making a total of 35, all of which are included in the two diagrams.

The larger part of the data upon which the compilation is based are from the results of researches made in the Geophysical Laboratory, individual references to which will be omitted. The dotted curves showing the expansion of tridymite and cristobalite are from measurements by Le Chatelier. The melting-points of Al_2O_3 , MgO , and CaO were determined by Kanolt at the Bureau of Standards.

All of the compositions have been recalculated to a molar percentage basis, in order to bring out more clearly the regularities and analogies. The temperature scales of the two-component diagrams are all alike, and the base of each diagram is at $1,000^\circ$. In the three-component diagrams the principal temperatures (quintuple points, etc.) are given in figures opposite the curve-intersections to which they apply. The three-component triangles are of course only projections upon a horizontal plane of the space model of the fusion surface, in which temperature is laid off vertically. Inversion-points in the solid phases therefore do not appear; it is also not practicable, on account of the small size of the diagrams, to show the primary phases in each field, and various other important facts for which reference must be made to the original papers. The triangular projections do, however, give a good comparative view of the different systems.

Unfortunately, many of the three-component triangles must be left nearly bare of information, but it is to be hoped that the next few years will see many of these gaps filled. In these cases, as well as in the completed diagrams, I have indicated by letters the compositions of the principal natural minerals belonging to the system.

A study of the composition of the binary compounds of these oxides brings out an important generalization which may be stated as follows: The stable oxygenated compounds of the elements silicon, aluminum, magnesium, lime, and iron with one another are all made up of the *refractory oxides* of these elements in *simple proportions*, usually 1:1 or 2:1. This seems to be true quite regardless of what might be expected from valence relations of the

TABLE II.

Binary Compounds of the Common Refractory Oxides.

System.	Compound.	Mineral Name.	Ratio of Oxides.
<i>Stable Compounds.</i>			
SiO ₂ -Al ₂ O ₃	Al ₂ SiO ₅	Sillimanite	1 : 1
SiO ₂ -MgO	Mg ₂ SiO ₄	Forsterite	2 : 1
SiO ₂ -CaO	CaSiO ₃	Wollastonite	1 : 1
	Ca ₂ SiO ₄	—	2 : 1
Al ₂ O ₃ -MgO	MgAl ₂ O ₄	Spinel	1 : 1
Al ₂ O ₃ -CaO	CaAl ₂ O ₄	—	1 : 1
	Ca ₃ Al ₁₀ O ₁₅	—	3 : 5
	Ca ₂ Al ₆ O ₁₄	—	5 : 3
Fe ₂ O ₃ -FeO	Fe ₃ O ₄	Magnetite	1 : 1
<i>Mineral Compounds, Stability Unknown.</i>			
SiO ₂ -FeO	FeSiO ₃	Grünerite	1 : 1
	Fe ₂ SiO ₄	Fayalite	2 : 1
Al ₂ O ₃ -FeO	FeAl ₂ O ₃	Hercynite	1 : 1
Fe ₂ O ₃ -MgO	MgFe ₂ O ₄	Magnesioferrite	1 : 1
<i>Compounds Unstable at Melting-point.</i>			
SiO ₂ -MgO	MgSiO ₃	Enstatite	1 : 1
SiO ₂ -CaO	Ca ₃ SiO ₅	—	3 : 1
	Ca ₃ Si ₂ O ₇	—	3 : 2
Al ₂ O ₃ -CaO	Ca ₃ Al ₂ O ₆	—	3 : 1
Fe ₂ O ₃ -CaO	CaFe ₂ O ₄	—	1 : 1
	Ca ₂ Fe ₂ O ₅	—	2 : 1
Fe ₂ O ₃ -FeO	2FeO · 3Fe ₂ O ₃	—	2 : 3

TABLE III.

Ternary Compounds of the Common Refractory Oxides.

System.	Ternary Compounds.	Mineral.	Oxide Ratios.
SiO ₂ -Al ₂ O ₃ -CaO	CaSiO ₃ · Al ₂ SiO ₅	Anorthite	(1 : 1) : (1 : 1)
	CaSiO ₃ · CaAl ₂ O ₄	Gehlenite	(1 : 1) : (1 : 1)
SiO ₂ -MgO-CaO	CaSiO ₃ · MgSiO ₃	Diopside	(1 : 1) : (1 : 1)
	Ca ₂ SiO ₄ · Mg ₂ SiO ₄	Monticellite	(2 : 1) : (2 : 1)

TABLE IV.

System.	Compound.	Mineral.	Oxide Ratios.
SiO ₂ -Al ₂ O ₃ -Na ₂ O	Na ₂ SiO ₃ · Al ₂ SiO ₅	Nephelite	(1 : 1) : (1 : 1) : 0
	Na ₂ SiO ₃ · Al ₂ SiO ₅ · 2SiO ₂	Jadeite	(1 : 1) : (1 : 1) : 2
	Na ₂ SiO ₃ · Al ₂ SiO ₅ · 4SiO ₂	Albite (feldspar)	(1 : 1) : (1 : 1) : 4
SiO ₂ -Al ₂ O ₃ -K ₂ O	K ₂ SiO ₃ · Al ₂ SiO ₅	Kaliophilite	(1 : 1) : (1 : 1) : 0
	K ₂ SiO ₃ · Al ₂ SiO ₅ · 2SiO ₂	Leucite	(1 : 1) : (1 : 1) : 2
	K ₂ SiO ₃ · Al ₂ SiO ₅ · 4SiO ₂	Orthoclase (feldspar)	(1 : 1) : (1 : 1) : 4

elements concerned. The validity of this rule will be evident from Table II, a list of all of the known binary compounds of the common refractory oxides, separated into two classes: (1) those which are stable at their melting-points and below, (2) those which dissociate at temperatures below their melting-points. Certain mineral compounds, whose properties are not yet well known, are also included.

It is interesting to note also that the majority of the compounds which are unstable at their melting-points contain a larger number of the individual molecules than do the stable compounds.

A generalization similar to the one stated above for binary compounds applies to the ternary compounds, as far as these are known. It may be stated thus: the ternary compounds of the common refractory oxides are made up of the more stable binary compounds (usually 1:1 compounds) in simple proportions, usually 1:1. This fact is illustrated by Table III, which contains all of the known compounds in two of the ternary systems which have been more or less completely studied.

An excursion into the field of the alkali silicates furnishes other interesting examples of this principle, as shown in Table IV.

The Silicates as "Molecular Compounds."

The whole impression left by a review, such as that outlined above, of the silicates and other compounds of the refractory oxides, is that these compounds are really "*molecular compounds*" of the oxides—in Werner's terminology, compounds of second and third order.

Students of the history of chemistry will recognize in this viewpoint something similar to the dualistic system of Berzelius, which flourished over one hundred years ago. But it differs radically from Berzelius's system, in that the idea that there must be a positive and negative part to every molecule is dropped. Long after its electrical basis was shown to be false, Berzelius's system persisted because of its convenience in the classification of chemical substances. The rise of the idea of valence, however, and the remarkable growth of organic chemistry with its basis in the structural formulas of organic compounds, drove Berzelius's system into the background.

Of late years the importance of so-called "molecular compounds" has been gaining increased recognition. It has been realized that the valence theory and the structural formulas based thereon have been inadequate to represent vast numbers of compounds between individual molecules within each of which the valences seemed to be completely "satisfied." It was these compounds that called forth Werner's important work on the ammonia complexes, and his theory of principal and secondary valences, which he has applied to a great number of complex compounds, including crystalline hydrates.

In the meantime, however, the structural formula and fixed valence idea had been extended to the inorganic compounds, including even the little-known silicates. Inorganic chains and rings were more common in the textbooks twenty years ago than they are now, but they still survive. Nevertheless, I think it is a fair statement that little or no good resulted from the inorganic structural formulas—certainly nothing comparable with their yield in the organic field. The most of them represented no real facts about the substance. This is especially true of the silicates, where the attempt to extend the organic idea resulted principally in confusion. Perhaps the climax was reached in a recent book by W. and D. Asch, in which we are provided with structural formulas for window glass and Portland cement.

F. W. Clarke's recent Geological Survey Bulletin on "The Constitution of

the Natural Silicates" is based on the structural idea, and some of his formulas do have a defensible basis of fact. But the variance between the facts and the predictions that one might reasonably make from these structural formulas is very wide. One can sit down with a pencil and paper and construct on the valence basis a number of aluminum silicates, for example, of various empirical formulas and various constitutions for each formula, and any one of these would seem just as likely to occur as another. Yet the *only* aluminum silicate that forms at high temperatures, namely, sillimanite, Al_2SiO_5 , has to be laid aside by Clarke as possibly a "basic metasilicate," a term that calls to mind the unsorted dump heap of ferric hydrates, lead carbonates, and other muddy mixtures inherited from the days of "basic salts."

This case of aluminum silicate, from the point of view that I am trying to set forth, is comparatively simple. Al_2O_3 and SiO_2 , being alike in forming many stable compounds with MgO , CaO , and other bases, may be expected to form no very stable compounds with each other. If any compound is formed, the one most to be expected is that which contains the simplest ratio of the *oxides*, namely, 1 : 1. This is exactly the compound that does form. Its small margin of existence, furthermore, is indicated by the very slightly pronounced maximum in the melting curve (see Fig. 1), and by the appearance of crystals of its constituent oxides in its melt, suggesting dissociation very near its melting-point.

Are the "molecular compounds" drawing us away, then, from the atomic theory and the structural formula? It would be a misfortune if such were the result. The atomic theory need no longer be looked upon as a theory, but rather as an assemblage of well-proved facts, and all chemical theory must rest on the atom. The structural formula, furthermore, has proved too valuable in organic chemistry to be lightly laid aside. At the same time there must be something behind the regularities which appealed to Berzelius, and which form so simple a basis for the understanding of the compounds of the refractory oxides.

There exist a considerable variety of facts which lead unavoidably toward the belief that the simpler molecules retain a certain degree of individuality when they enter into the more complex compounds. Water of crystallization, for instance, shows the same spectral absorption bands as water in solid solution and as liquid water itself. It is not necessary to suppose, however, that there is any sharp division between "molecular" and "atomic" compounds, or between compounds of different "orders." We may rather expect that there is a continuous gradation from compounds in which the physical properties of the constituents have almost completely disappeared, over to the "weakest" of molecular compounds, where the physical properties of the constituent molecules are almost completely retained.

The Structure of Crystalline Compounds.

But no sooner have we convinced ourselves that certain molecules (such as the refractory oxides) retain a considerable degree of their individuality in crystalline compounds, than we are informed by the X-ray analysis of crystal structure that in a crystal the molecule has completely disappeared, or rather, we should say, the crystal itself is one huge molecule. The X-ray spectra of a crystal reveal to us that it consists only of *atoms*, arranged in space in an orderly manner. A crystal of sodium chloride, for instance, is only an assemblage of row upon row and layer upon layer of sodium and chlorine atoms, in which no particular sodium atom is united to any particular

chlorine atom. The word "molecule," in the case of crystalline sodium chloride, therefore, no longer represents any concept, as it does in the case of a gas. This apparently unavoidable deduction has been hard for some of the chemists to swallow, and they have sought ways of preserving the molecule in the crystal. Barlow,* for instance, believes that a sufficient degree of symmetry to explain the X-ray patterns can be obtained in a sodium chloride crystal by an arrangement of the atoms which still permits a given sodium atom to lie nearer to one particular chlorine atom than to any other chlorine, so that these pairs may still be considered real molecules in the crystal.

Whether our familiar concept of the molecule will survive, when applied to the crystalline state, is for the future to determine. For the present we

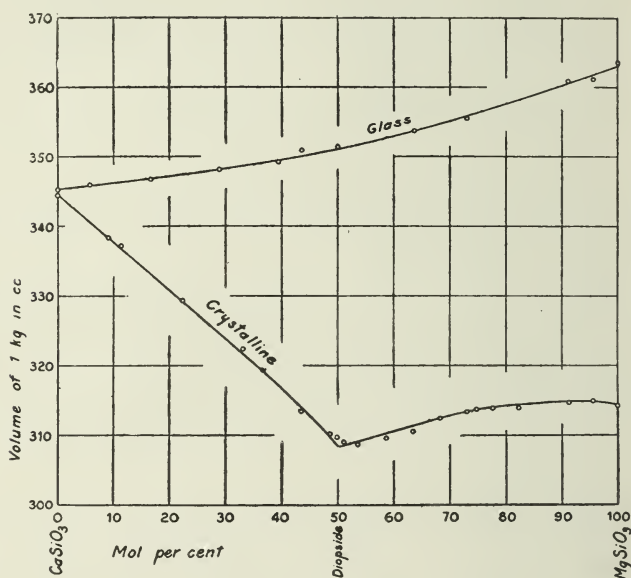


FIG. 3.

may content ourselves with the conviction that the molecule is at least *potentially* present, for let the crystal of sodium chloride be heated to its melting-point, then each sodium atom will seize upon a chlorine atom and go whirling away with it into the liquid, like the individuals in a ballroom who have been sitting quietly on orderly rows of chairs until the music starts, when they suddenly group themselves into pairs which go circling about the room.

There is considerable evidence, on the other hand, that certain compounds that exist in the crystalline state are entirely dissociated in the liquid state. The concept of molecule, as applied in the liquid and gaseous states, can therefore have no meaning at all in the case of these compounds. Their formation must be controlled by forces which come into play only when the atoms arrange themselves in orderly patterns; they may be considered to be not the result of chemical affinities or valences between atoms, as we ordinarily understand such forces in a liquid or gaseous molecule, but merely the

* *Proc. Roy. Soc.* **91** (1914), 1-16.

result of the fact that an orderly arrangement of atoms has been brought about. In other words, the occurrence of a melting-point maximum and the other indications of one of these compounds in the phase-rule diagram might have been predicted, not by chemistry, but by geometry. The silicate diopside, $\text{CaSiO}_3 \cdot \text{MgSiO}_3$, for instance, may be such a compound. Fig. 3 gives the curves of specific volume against composition for all mixtures of CaSiO_3 and MgSiO_3 , both in the glassy and in the crystalline state. There is no indication of the existence of a compound in the liquid (unordered or glassy) state. Only when the glass is crystallized does the sharp maximum of condensation appear at the composition 1 : 1.

Practical Aspects.

There are certain principles of practical importance which may be deduced from the facts presented in Figs. 1 and 2. In the first place it will be observed that the maximum melting-points in all of the two- and three-component systems are the melting-points of pure stable compounds, and the highest melting-points of all are those of the pure oxides, Al_2O_3 , CaO , and MgO . This fact is of particular importance to the maker of refractory mixtures. In general, it may be said that the addition of any substance to a refractory will tend to lower its melting-point. One principal line of progress in refractories must lie, therefore, in the direction of greater chemical purity in the materials.

Of course, high melting-point is not the only desirable feature of a refractory, nor is it always the most desirable. The raw material must be easily moulded or cast and easily bonded, and the product must be mechanically strong. In order to get the material bonded and to give it strength and resistance to abrasion, it is customary to add a bonding material. The Norton Company's alundum wares, for instance, contain a variable quantity of a silicious cement. The result is a troublesome shrinkage at temperatures far below the melting-point of the alumina, which is the principal constituent of the ware; this shrinkage is caused by the combining of SiO_2 with Al_2O_3 and perhaps with other impurities present, and the flowing of the resulting viscous liquid.

An instance of the refractoriness of a pure compound is furnished by the very successful "Marquardt Porcelain" made by the Royal Berlin Porcelain Works. The mineral kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, the principal constituent of fire-clay, is not the hydrate of any high-temperature compound, and when it is heated it breaks up. At high temperatures it becomes then simply a mixture of Al_2SiO_5 and SiO_2 , which if heated for a long time will soften and flow at the temperature of the eutectic between Al_2SiO_5 and SiO_2 , which is lower even than the melting-point of SiO_2 , or below $1,625^\circ$. But if Al_2O_3 is added to a pure kaolin to make a mixture equivalent in composition to Al_2SiO_5 , which is the pure compound sillimanite, then at a high temperature this compound will form. Once formed, it will not melt or flow below $1,815^\circ$.

This is not, of course, the whole story of Marquardt porcelain. Grinding, mixing, moulding, drying, and burning all introduce their difficulties, but the fundamental principle remains that all these processes are directed towards the building of a pure high-melting compound.

An interesting phenomenon exhibited by the refractory oxides is that known as sintering. Any finely powdered substance if held slightly below its melting-point will sinter together more or less solidly. The nearer to its melting-point an object made of a pure refractory oxide can be burned, therefore, the less binder it will require. There is no reason why a perfectly pure oxide, such as Al_2O_3 , cannot be made into a dense hard refractory

without the aid of any bond, provided only that the temperature is under good control.*

Another method of bonding a refractory has been already hinted at in the description of Marquardt porcelain. If a pure high-melting compound of two or more oxides be selected as the refractory, it may be made up by thoroughly mixing the component oxides in finely powdered form. The mixture is then moulded in the usual way, dried, and burned. At a temperature well below the melting-point of the compound, the oxides will begin to unite to form the compound, and this chemical reaction will bind the mass together even more effectively than could be accomplished by sintering.

The best example of such a product is magnesium aluminate or spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$. It has been occasionally used by individual investigators in Germany for crucibles, tubes, and the like, and a similar mixture, probably impure, has also been made up into forms by the Royal Berlin Porcelain Works. As is shown in Fig. 1, its melting-point is unusually high and its eutectics with its two component oxides melt not much lower ($1,925^\circ$ and $2,030^\circ$). Particular care need not be taken, therefore, to make it up in the exact proportion to form $\text{MgO} \cdot \text{Al}_2\text{O}_3$. It is to be regretted that it is not yet available in this country in forms similar to those of Norton alundum.

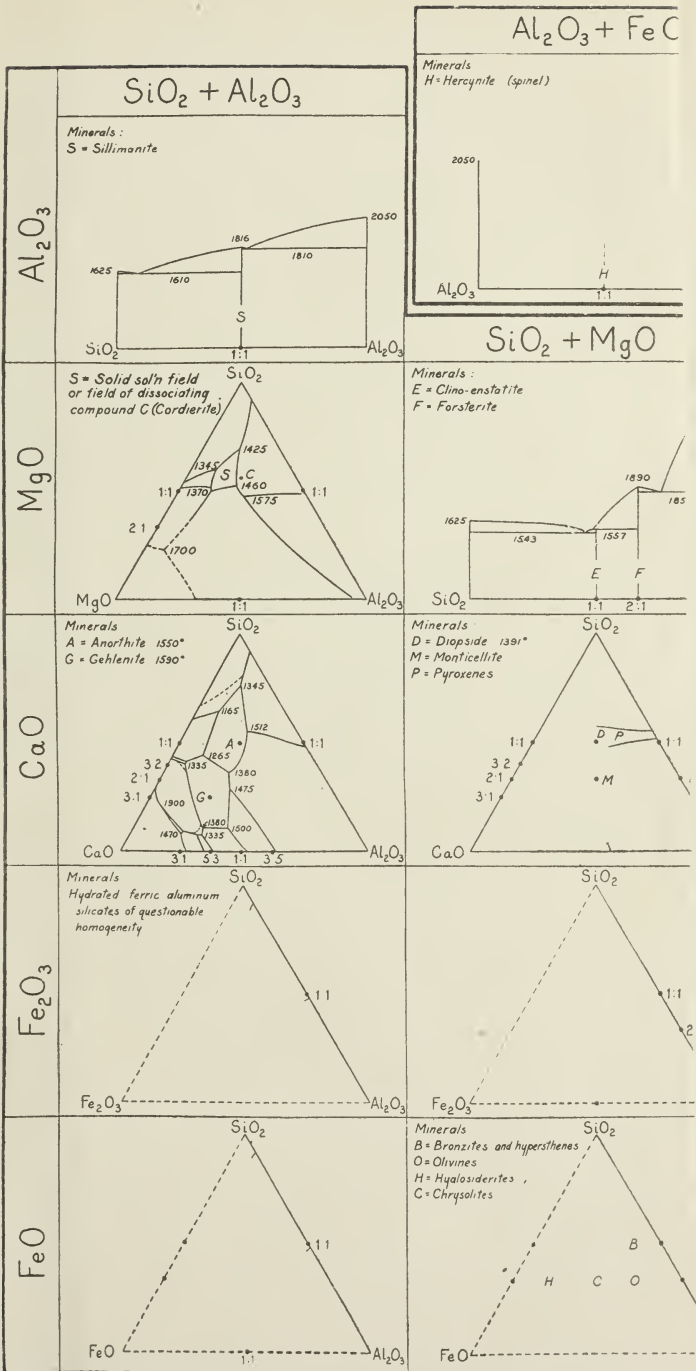
Among the other facts represented on the diagrams of Figs. 1 and 2 which find applications in industrial science, we may mention some of the properties of the polymorphic forms of the pure oxides. One of the diagrams of Fig. 2 represents the volume curves of the forms of silica. The inversion of quartz at 575° is accompanied by a sudden change of volume, an expansion in passing from the low- to the high-temperature form; so a granite wall in a burning building, if it becomes heated to 575° , is seriously shattered by the inversion of the quartz which makes so large a proportion of the stone. The silica-brick cap of a glass furnace, as the temperature passes 575° , changes so rapidly in dimensions that a man must be kept at hand with a wrench to "follow up" the cap. No ordinary force is able to resist the change; a pile of 4 or 5 tons of pig iron failed to keep the cap from rising at 575° .† Another practical effect is the disintegration of silica brick. Brick made of quartz is likely to be "rotted" or weakened by disintegration if heated and cooled repeatedly past the 575° point.

Fused silica, or "quartz glass," is only stable above the melting-point of cristobalite ($1,625^\circ$). If used at temperatures below this, it strives constantly to crystallize, and the speed of crystallization is greater the higher the temperature. Hence the well-known "devitrification" of silica glass. But it happens that the high-temperature form of cristobalite has practically the same density as the glass itself, so that if held at a high temperature the material retains its transparency and homogeneity. Only when it passes the α - β inversion-point at 200° to 275° does it break up into the familiar chalky, devitrified mass. Whether the cristobalite retains the strength of the glass at high temperatures I do not know, but for some purposes, at least, it might be interesting to see whether the original advantageous properties of the glass would not be preserved if the furnace were not allowed to cool below 300° .

In 1914 Mr. F. J. Tone, of the Carborundum Company, sent us what seemed to be a new crystalline form of silica, consisting of a chalky mass

* In the discussion of the paper in America, Mr. Landis stated that in attempting to carry out the Caro process for the oxidation of ammonia, catalysers of cerium oxide, of thorium oxide, and of various mixtures of these oxides had been tried, and that at a temperature below 800° all of these oxides sintered to an impervious mass on long-time runs.

† *Trans. Am. Cer. Soc.*, 15 (1913), 519.



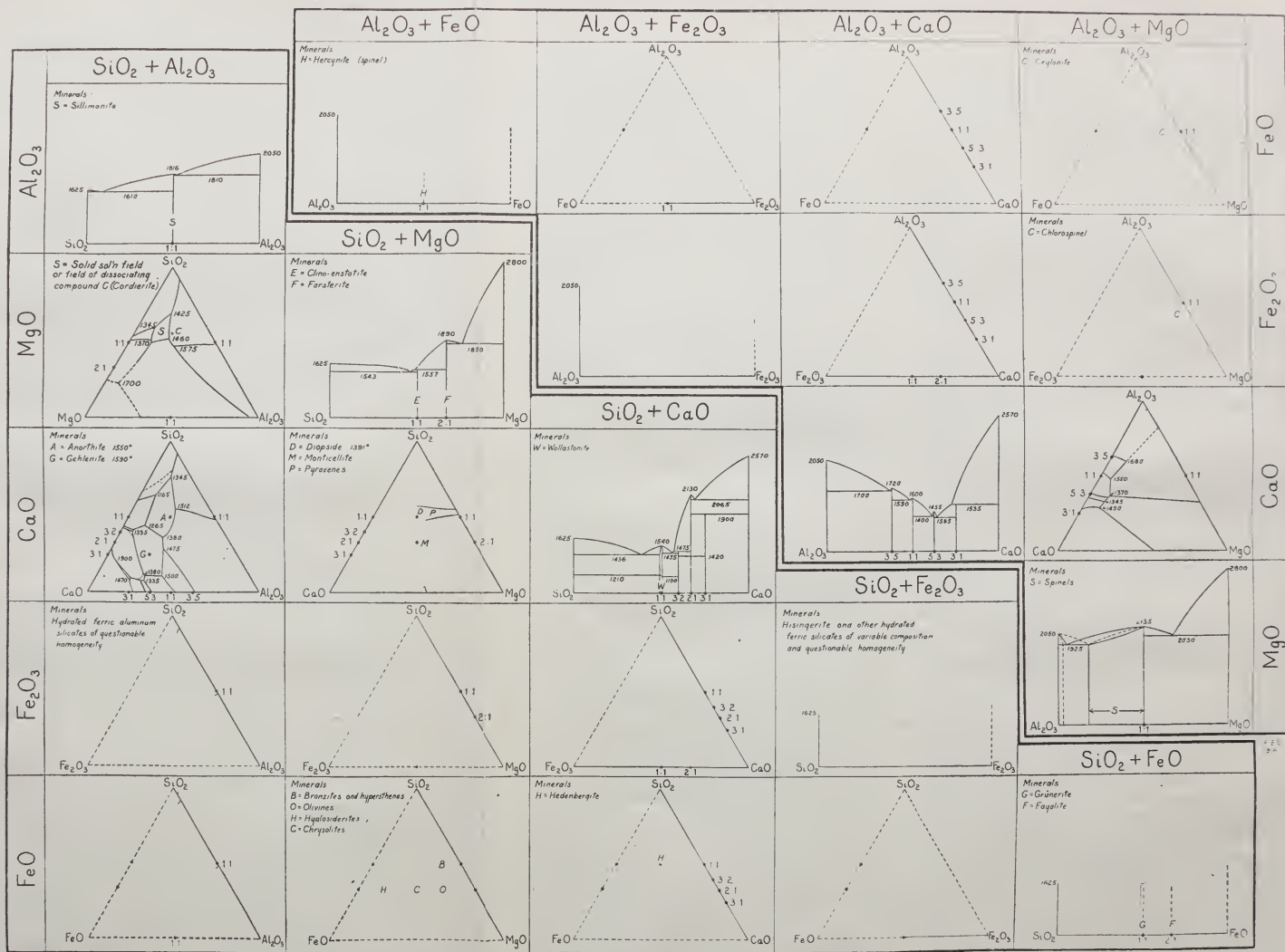
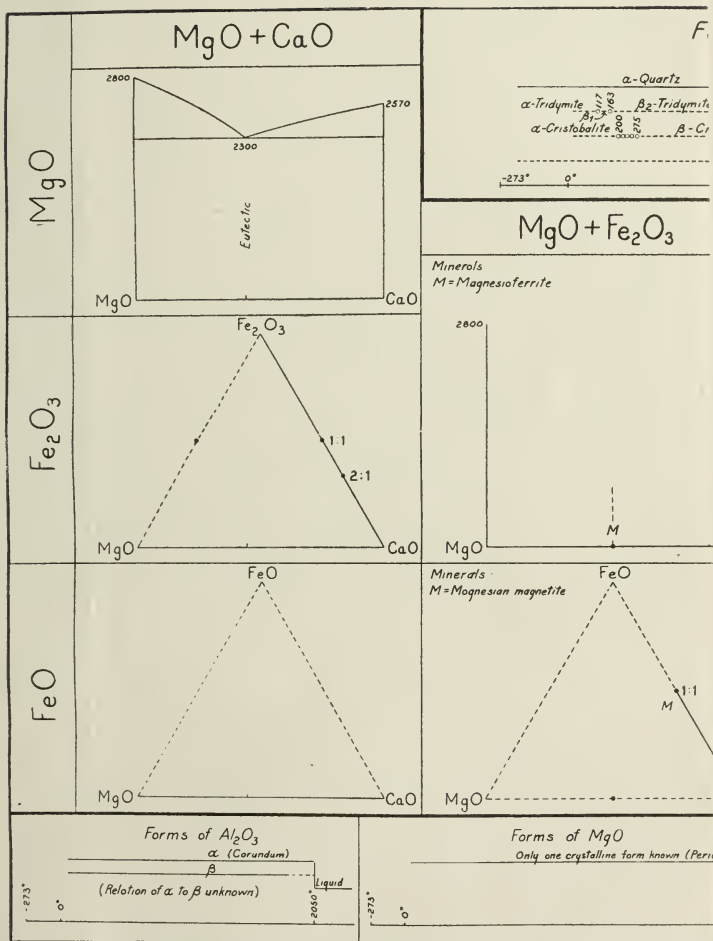


FIG. 1.



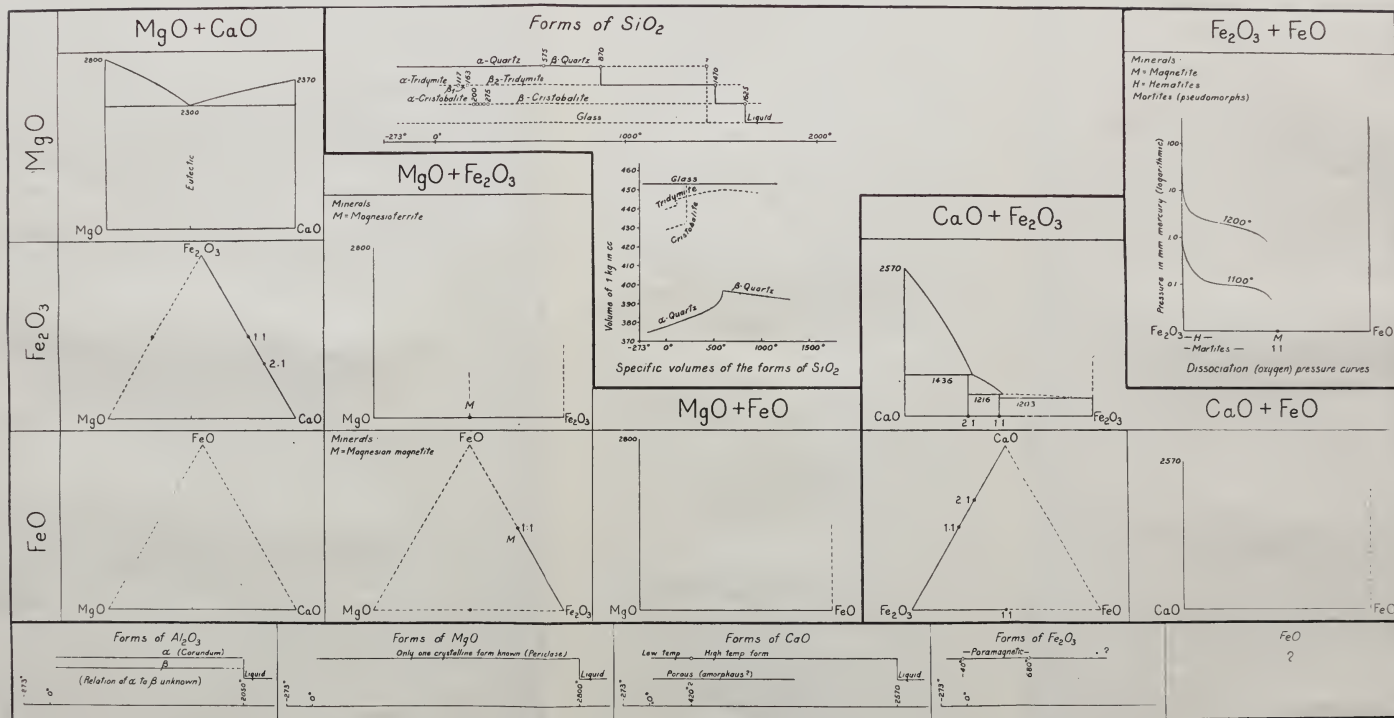


FIG. 2.

of fine parallel fibres. The microscope showed that it was really amorphous, and was, in fact, a *fibrous glass*, probably deposited from a vapour. This tendency of amorphous silica to deposit in various fibrous forms is very marked.

Crystalline alumina is now used by the hundreds of tons in grinding-wheels. The crystals are for the most part corundum or α -alumina, but a certain proportion of β -alumina is also found in the artificial abrasives. One use of this fused alumina which is familiar to all chemists is in the Norton Company's "alundum" articles. We have observed recently that boats made of alundum are extraordinarily constant in weight at high temperatures, much more so than platinum.* Platinum steadily loses weight in oxygen at 1,100–1,200°, especially when iron oxide is heated in it, whereas an alundum boat is constant within 0.1 mg. The reason is simple and obvious: platinum is an oxidizable metal and forms a volatile oxide, while alumina is a completely saturated and non-volatile oxide. At 1,100–1,200° the platinum is oxidized by the oxygen of the air, and the oxide is carried away, while the Al_2O_3 remains unchanged.

Many other facts with their practical applications could be brought out by going through the diagrams in detail, but I believe that enough has been said to show that future progress in the application of our knowledge of the common refractory oxides must follow two principal lines: (1) *control of the purity of materials*, and (2) *accurate control of high temperatures*.

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* Hostetter and Sosman, *Journ. Am. Chem. Soc.*, **38** (1916), 1188–98.

APPENDIX I

STANDARD SPECIFICATIONS FOR REFRACTORY MATERIALS.*

These Specifications have already been issued in sections to form part of the reports which the Refractory Materials Committee of the Institution have made from time to time, and it is now deemed advisable to assemble them.

It was explained in the reports mentioned that the details of the Specifications have been the work of a Joint Committee formed of representatives of the Refractory Materials Committee and of the Retort and Firebrick Section of the Society of British Gas Industries, and the clauses as drawn up were unanimously agreed to be fair and reasonable both to purchaser and to manufacturer. Dr. H. G. Colman, D.Sc., acted as Chairman of this Sub-Committee, and Dr. J. W. Mellor, D.Sc., the Principal of the Staffordshire County Pottery Laboratory, as its Technical Adviser.

In the spring of 1910 the Refractory Materials Committee instituted an inquiry into the temperatures then being used in retort settings and carburetted water gas plants, and carefully compiled data relating thereto were obtained from representative gas undertakings. This information formed a most valuable and accurate guide when deciding upon the various tests. The subsequent method followed in the preparation of all the sections of the Specification, was to obtain samples of material from a large number of representative firms for testing purposes, and due regard was paid to the results obtained when deciding upon the terms of the Specification. The reason for this is obvious; for, however desirable, no violent departure from the established practice of the manufacturers could hope to succeed or obtain their support; and happily this is not necessary, for the tests which the Committee have had carried out reveal the fact that excellent material is available, and only more selection and attention to certain features is necessary in order to obtain very much improved results.

The Specifications have been drawn up with as little reference as possible to details of manufacture, in which it is thought those responsible should be allowed considerable latitude to employ any methods or mixtures they think desirable. The Committee would, however, draw attention to the test for porosity in the Specification for retort material. The repeated changes of temperature to which retorts are subjected are a frequent cause of failure, and the material should therefore, in addition to being highly refractory, have an open, porous texture, and should at the same time show little expansion or contraction when heated to a high temperature.

It is not suggested that finality has been reached with these Specifications, and it may be necessary to revise them and add other clauses and tests from time to time. Sufficient experience has already been obtained, however, to enable the Committee to state that very considerable improvement in the quality and uniformity of refractory materials will be obtained from their use,

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and it is also held that the manufacturer will benefit very much by reason of the fact that he will have some definite standard to which to work.

It should, however, be pointed out to Engineers adopting them, both in justice to those manufacturers who are prepared to work carefully to the Specifications, as also to the Committee responsible for their preparation, that it is necessary to take care that they are strictly adhered to, and that the material purchased in accordance therewith is subjected to the tests specified. It is only in this way that continued improvement in the quality of retort and firebrick material is to be expected.

SECTION 1.—RETORT MATERIAL.

SPECIFICATION.

CONSTITUENTS.

Clause 1.—The retorts or retort tiles shall be made of sufficiently seasoned raw clay and clean burnt clay or "grog." No "grog" shall be used which will pass through a test sieve having 16 meshes to the linear inch.

CHEMICAL ANALYSIS.

Clause 2.—A complete chemical analysis of the material is to be provided when required by the engineer (or purchaser), for his personal information only.

REFRACTORINESS.

Clause 3.—A piece of the material shall show no signs of fusion when heated to a temperature of not less than Seger cone 28 (about 1,630° C.) in an oxidizing atmosphere; the heat being increased at the rate of about 50° C. per five minutes.

[NOTE.—The new scale of Seger cones printed in the Appendix is to be used.]

SURFACES AND TEXTURE.

Clause 4.—All surfaces shall be reasonably true and free from flaws or winding; and, after burning, no "washing" shall be done without the consent of the engineer (or purchaser). The texture throughout shall be even and regular, containing no holes or flaws, and the "apparent porosity" shall not be less than 18 per cent.

CONTRACTION.

Clause 5.—The material shall be evenly burnt throughout, and contain no black core. A test-piece, when heated to a temperature of Seger cone 14, for two hours, shall not show, when cold, more than $1\frac{1}{4}$ per cent. contraction or expansion. After the test temperature has been obtained the furnace shall be maintained at a constant temperature throughout the testing period. The test-piece shall be $4\frac{1}{2}$ in. long by $4\frac{1}{2}$ in. wide and representative of the whole piece of retort or retort tile from which it is taken; the ends shall be ground flat, and the contraction measured by means of Vernier callipers reading to 0.1 mm.—a suitable mark being made on the test-piece, so that the callipers may be placed in the same position before and after firing.

INSPECTION AND TESTING.

Clause 6.—The engineer (or purchaser) or his agreed representative shall have access to the works of the maker at any reasonable time, and shall be at liberty to inspect the manufacture at any stage, and to reject any material which does not conform to the terms of this specification. Pieces, representative of the bulk, may be selected for the purpose of testing, either before or after delivery; but in either case a representative of the maker shall, if he choose, be present when such selection is made, and shall be supplied with a similar piece of the retort material to that taken for the purpose of testing. Any complaint as to quality of the material to be made by the purchaser before the expiration of ten days after delivery.

If the engineer (or purchaser) and the maker are not prepared to accept each other's tests, they shall agree to submit the samples for testing to an independent authority to be mutually agreed upon; and the engineer (or purchaser) reserves to himself the right, if the material does not conform to the tests laid down in the specification, to reject any or all the material in the consignment from which the test-pieces were taken.

The cost of these independent tests, and of any retort lengths or tiles damaged before delivery for obtaining test-pieces, shall be equally divided between the purchaser and the maker if the test proves satisfactory; and if unsatisfactory, such cost, and that for all other subsequent tests required on this account from the same consignment, shall be borne by the makers.

The cost of any tests or of any material damaged for the purpose of obtaining test-pieces after delivery shall be borne by the purchaser in the event of the test being satisfactory, and if unsatisfactory by the manufacturer, in a similar manner to that specified for the tests prior to delivery.

APPENDIX AND NOTES.

CONSTITUENTS.

Clause 1.—The sieve to be used is the test-sieve specified by the Institute of Mining and Metallurgy.

CHEMICAL ANALYSIS.

Clause 2.—The silica should be determined by two evaporations with an intervening filtration; and the alumina, lime, and magnesia, by two precipitations. The amount of titanite oxide should be indicated, and not confused with alumina and iron. The potash and soda should be separately determined.

REFRACTORINESS.

Clause 3.—The Deville furnace, although useful for comparative tests in refractoriness, is not altogether suitable for carrying out those specified in this clause, for which a compressed air-gas furnace of the Méker type, or Hirsch's electric furnace, is recommended. The latter can be obtained from Messrs. Gallenkamps, of London; the former from the Scientific Instrument Company, of Cambridge. The gas-furnace will require an air-pressure of at least 10 lb. per square inch; and for the electric furnace a current of approximately 90 volts and 90 amps., with a slightly higher voltage at the start, has been found, by means of a carefully standardized Wanner pyrometer, to be sufficient.

Two or more tests are generally required with an unknown material.

A preliminary trial is first made with a piece of the material chipped into the approximate form of a cone. This should be cemented on to a refractory disc or slab with a mixture of alumina and best china clay, together with Seger cones 28, 30, and 32 (small size). These cones are selected because they cover the range of first-grade clays usually employed for retort material. Best china clay fuses between cones 35 and 36; and all British fire-clays fall below this point. If cones 28 and 30 fall, the furnace should be cooled, and the material under investigation examined. If it exhibits no sign of fusion, the trial should be repeated with cones 31, 32, and 33. When cone 32 squats, the piece should be again examined; and if it shows signs of fusion, the trial should be repeated with cones 30, 31, and 32. By this method of approximation, it is possible to decide whether the piece vitrified between cones 30 and 31 or between cones 31 and 32. The cones should in all cases be placed relative to the sample, so that both are subjected to the same temperature.

It should be noted that clays and related materials have no sharply defined melting-points, and the definition of refractoriness here adopted refers to the temperature at which the angular edges of the material under investigation begin to lose their angularity when heated under the conditions stated.

SOFTENING POINTS OF SEGER CONES.

Cone No.	Cent.	Fahr.	Cone No.	Cent.	Fahr.
022	600	1,112	9	1,280	2,336
021	650	1,202	10	1,300	2,372
020	670	1,238	11	1,320	2,408
019	690	1,274	12	1,350	2,462
018	710	1,310	13	1,380	2,516
017	730	1,346	14	1,410	2,570
016	750	1,382	15	1,435	2,615
015a	790	1,454	16	1,460	2,660
014a	815	1,499	17	1,480	2,696
013a	835	1,535	18	1,500	2,732
012a	855	1,571	19	1,520	2,768
011a	880	1,616	20	1,530	2,786
010a	900	1,652	26	1,580	2,876
09a	920	1,688	27	1,610	2,930
08a	940	1,724	28	1,630	2,966
07a	960	1,760	29	1,650	3,002
06a	980	1,796	30	1,670	3,038
05a	1,000	1,832	31	1,690	3,074
04a	1,020	1,868	32	1,710	3,110
03a	1,040	1,904	33	1,730	3,146
02a	1,060	1,940	34	1,750	3,182
01a	1,080	1,976	35	1,770	3,218
1a	1,100	2,012	36	1,790	3,254
2a	1,120	2,048	37	1,825	3,317
3a	1,140	2,084	38	1,850	3,362
4a	1,160	2,120	39	1,880	3,416
5a	1,180	2,156	40	1,920	3,488
6a	1,200	2,192	41	1,960	3,560
7	1,230	2,246	42	2,000	3,632
8	1,250	2,282			

APPARENT POROSITY.

Clause 4.—The “apparent porosity” tells what fraction of the volume of the whole piece is occupied by air-spaces, and is therefore :—

$$\frac{\text{Volume of pores} \times 100}{\text{Volume of piece (including pores)}}$$

This constant can be determined in one of the numerous voluminometers working with the vacuum process. Messrs. Gallenkamp & Co., of London, made a porosimeter which allows of this determination being made as quickly as is consistent with accuracy. The details of working are supplied with the instrument.

LINEAR CONTRACTION OR EXPANSION.

Clause 5.—The term “linear contraction or expansion” indicates the percentage change in length (and by a simple calculation the change in volume) which occurs when a piece is tested under the conditions stated. Consequently the linear contraction or expansion is :—

$$\frac{\text{Change in length} \times 100}{\text{Original length of piece}}.$$

A carborundum wheel may be used for grinding the ends of the test-pieces flat, and a mark should be made across the slab with a steel file. One of the Méker gas-furnaces, with blast if necessary, may be used for carrying out the test. The test-piece should be supported horizontally, and fired along with cones 13, 14, and 15.

As soon as cone 14 has squatted, it ceases to furnish any further indication of the temperature of the muffle ; so that the subsequent temperatures should be ascertained, at about 15-minute intervals, by means of a pyrometer. It is essential, however, that the temperature should be maintained constant ; and if it is necessary to remove plugs, etc., for the purpose of obtaining the temperature, great care must be taken to avoid cooling the furnace by such means. As in the test for refractoriness, the cones should be placed in such a position relative to the sample under test, that both may be subjected to the same temperature.

INSPECTION AND TESTING.

Clause 6.—It has been pointed out by the representatives of the manufacturers that, owing to the high cost of carriage, they may be involved in serious loss if material is extensively rejected after delivery. They agree that the purchaser must have entire freedom to test, and reject, if necessary, any material delivered to him ; but it is suggested that, until all the manufacturers have suitable arrangements and appliances for constantly testing their goods, it may be possible to render them some assistance by allowing a fairly large sample of their material to be sent in for testing and general approval before extensive deliveries are made. This is in no way, however, to be construed as removing the right of the purchaser to test material in any subsequent consignment.

SECTION 2.—FIREBRICKS, BLOCKS, TILES, Etc.

SPECIFICATION.

PREAMBLE.

For the purpose of classification, it is understood that this specification applies generally to material made from fire-clay containing approximately not more than 75 per cent. of silica. It is known, however, that there are in certain areas fire-clays containing as much as 80 per cent. silica ; and material made from such clays shall be considered to conform to this specification if it passes the tests herein specified.

REFRACTORINESS.

Clause 1.—Two grades of material are covered by the specification.

- (1) Material which shows no sign of fusion when heated to a temperature of not less than Seger cone 30 (about 1,670° C.).
- (2) Material which shows no sign of fusion when heated to a temperature of not less than Seger cone 26 (about 1,580° C.).

The test shall be carried out in an oxidizing atmosphere, the temperature of the furnace being increased at the rate of about 50° C. per five minutes.

[NOTE.—The new scale of Seger cones printed in the Appendix to Section 1 is to be used.]

CHEMICAL ANALYSIS.

Clause 2.—A complete chemical analysis of the material is to be provided when required by the engineer (or purchaser), for his personal information only.

SURFACES AND TEXTURE.

Clause 3.—The material shall be evenly burnt throughout, and the texture regular, containing no holes or flaws. All surfaces shall be reasonably true and free from flaws or winding.

CONTRACTION OR EXPANSION.

Clause 4.—A test-piece when heated to a temperature of Seger cone 14 for two hours shall not show more than the following linear contraction or expansion :—

No. 1 grade, 1 per cent.

No. 2 grade, 1.25 per cent.

After the test temperature has been obtained the furnace shall be maintained at a constant temperature throughout the test period. The test-piece shall be $4\frac{1}{2}$ in. long by 4 in. wide, and representative of the whole piece of material from which it is taken; the ends shall be ground flat, and the contraction measured by means of Vernier callipers reading to 0.1 mm.—a suitable mark being made on the test-piece, so that the callipers may be placed in the same position before and after firing.

VARIATIONS FROM MEASUREMENTS.

Clause 5.—In the case of ordinary bricks, 9 in. by $4\frac{1}{2}$ in. by 3 in. or $2\frac{1}{2}$ in. thick, there shall not be more than $\pm 1\frac{1}{2}$ per cent. variation in length, nor more than $\pm 2\frac{1}{2}$ per cent. variation in width or thickness; and in all cases the bricks shall work out their own bond, with not more than $\frac{1}{8}$ -in. allowance for joint. In the case of special bricks, blocks, or tiles, there shall not be more than ± 2 per cent. variation from any of the specified dimensions.

CRUSHING STRENGTH.

Clause 6.—The material shall be capable of withstanding a crushing strain of not less than 1,800 lb. per square inch, when applied in the manner set out in the appendix.

CEMENT CLAY.

Clause 7.—This shall be machine ground, and at the discretion of the manufacturer may contain a suitable percentage of fine "grog." But in all

cases the cement clay shall be quite suitable for the purpose of binding together the bricks, blocks, or tiles for which it is supplied, and shall be capable of withstanding the same test for refractoriness.

MARKING OF MATERIAL.

Clause 8.—All bricks, blocks, or tiles shall be distinctly marked by means of a figure 1 or 2 (not less than 1 in. long) stamped on them to indicate the grade to which they belong, and it shall be understood that any material not so marked is ungraded, and is not purchased in accordance with the terms of this specification.

INSPECTION AND TESTING.

Clause 9.—The engineer (or purchaser), or his agreed representative shall have access to the works of the maker at any reasonable time, and shall be at liberty to inspect the manufacture at any stage, and to reject any material which does not conform to the terms of this specification. Pieces representative of the bulk may be selected for the purpose of testing, either before or after delivery; but in either case a representative of the maker shall, if he choose, be present when such selection is made, and shall be supplied with a similar piece of the material to that taken for the purpose of testing. Any complaint as to the quality of material to be made by the purchaser before the expiration of ten days after delivery.

If the engineer (or purchaser) and the maker are not prepared to accept each other's tests, they shall agree to submit the samples for testing to an independent authority to be mutually agreed upon; and the engineer (or purchaser) reserves to himself the right, if the material does not conform to the tests laid down in the specification, to reject any or all the material in the consignment from which the test-pieces were taken.

The cost of these independent tests and of any bricks, blocks, or tiles damaged before delivery for obtaining test-pieces, shall be equally divided between the purchaser and the maker if the test proves satisfactory; and if unsatisfactory, such cost, and that for all other subsequent tests required on this account from the same consignment, shall be borne by the makers.

The cost of any tests or of any material damaged for the purpose of obtaining test-pieces after delivery shall be borne by the purchaser in the event of the test being satisfactory, and if unsatisfactory by the manufacturer, in a similar manner to that specified for the tests prior to delivery.

APPENDIX AND NOTES.

For Table giving the approximate temperatures of the softening points of Seger cones, also for suggestions as to the general method of making chemical analyses and carrying out the tests for refractoriness, and contraction or expansion, etc. see notes under this heading in the Appendix to Section I.

CRUSHING STRENGTH.

Clause 6.—The machine required for the measurement of the crushing strength is so expensive that it will generally be necessary to have the tests carried out in a suitably equipped laboratory. The method to be employed is often determined by the capacity of the machine. The measurements on which the datum stated in the specification was based, were made in a large Avery machine, with whole bricks placed with their long side vertical

between the jaws of the machine, giving a vertical thrust. The most important factors requiring attention are :—

- (1) The two ends of the brick which come in contact with the jaws of the machine must be either ground or sawn flat and parallel, so as to receive a vertical thrust.
- (2) An average of not less than three bricks must be used, because flaws, etc., may give an abnormal result, which might not be detected if only one brick be used.

SECTION 3.—SILICA BRICKS, BLOCKS, TILES, Etc.

The material covered by this specification is divided into two classes :—

- (1) That containing 92 per cent. and upwards of silica, and hereinafter called "silica" material.
- (2) That containing from 80 to 92 per cent. of silica, and hereinafter called "siliceous."

REFRACTORINESS.

Clause 1.—Test-pieces of the material shall show no sign of fusion when heated to the following temperatures :—

"Silica" material—not less than Seger cone 32 (about 1,710° C.).

"Siliceous" material—not less than Seger cone 29 (about 1,650° C.).

The test shall be carried out in an oxidizing atmosphere ; the temperature of the furnace being increased at the rate of about 50° C. per five minutes.

[NOTE.—The new scale of Seger cones printed in the Appendix to Section I is to be used.]

CHEMICAL ANALYSIS.

Clause 2.—A complete chemical analysis of the material is to be provided when required by the engineer (or purchaser) for his personal information only.

SURFACES AND TEXTURE.

Clause 3.—The material shall be evenly burnt throughout, and the texture regular, with no holes or flaws. All surfaces shall be reasonably true and free from flaws or winding.

CONTRACTION AND EXPANSION.

Clause 4.—A test-piece, when heated in a gas-muffle or electric furnace to a temperature of Seger cone 12 for two hours shall not show, on cooling, more than 0.75 per cent. linear contraction or expansion. The temperature of the furnace shall be maintained constant throughout the testing period ; and the test-piece shall be at least 4½ in. long by 4½ in. wide—the ends being ground flat, and the contraction or expansion measured by means of Vernier callipers reading to 0.1 mm.—a suitable mark being made on the test-piece, so that the callipers may be placed in the same position before and after firing. The test sample shall not be taken out of the middle of a brick, block, or tile, but shall be representative of the whole.

VARIATIONS FROM MEASUREMENTS.

Clause 5.—In the case of ordinary bricks, 9 in. by 4½ in. by 3 in. or 2½ in. thick, there shall not be more than $\pm 1\frac{1}{2}$ per cent. variation in length, nor more than $\pm 2\frac{1}{2}$ per cent. variation in width or thickness; and in all cases the bricks shall work out their own bond. Special bricks, blocks, or tiles shall not have more than ± 2 per cent. variation from any of the specified dimensions.

CEMENT CLAY.

Clause 6.—This shall be machine ground, and at the discretion of the manufacturer may contain a suitable percentage of fine "grog." But in all cases the cement clay shall be quite suitable for the purpose of binding together the bricks, blocks, or tiles, for which it is supplied, and shall be capable of withstanding the same test for refractoriness.

INSPECTION AND TESTING.

Clause 7.—The engineer (or purchaser), or his agreed representative, shall have access to the works of the maker at any reasonable time, and shall be at liberty to inspect the manufacture at any stage, and to reject any material which does not conform to the terms of this specification. Pieces representative of the bulk may be selected for the purpose of testing either before or after delivery; but in either case a representative of the maker shall, if he choose, be present when such selection is made, and shall be supplied with a similar piece of the material to that taken for the purpose of testing.

Any complaint as to quality of material to be made by the purchaser before the expiration of ten days after delivery.

If the engineer (or purchaser) and the maker are not prepared to accept each other's tests, they shall agree to submit the samples for testing to an independent authority to be mutually agreed upon; and the engineer (or purchaser) reserves to himself the right, if the material does not conform to the tests laid down in the specification, to reject any or all the material in the consignment from which the test-pieces were taken.

The cost of these independent tests and of any bricks, blocks, or tiles, damaged before delivery for obtaining test-pieces, shall be equally divided between the purchaser and the maker if the test proves satisfactory; and if unsatisfactory, such cost, and that for all other subsequent tests required on this account from the same consignment, shall be borne by the makers.

The cost of any tests or of any material damaged for the purpose of obtaining test-pieces after delivery shall be borne by the purchaser in the event of the test being satisfactory, and if unsatisfactory by the manufacturer, in a similar manner to that specified for the tests prior to delivery.

APPENDIX AND NOTES.

For Table giving the approximate temperatures of the softening points of Seger cones, also for suggestions as to the general method of making chemical analyses and carrying out the tests for refractoriness, and contraction or expansion, etc., see notes under this heading in the Appendix to Section 1.

APPENDIX II

GENERAL DISCUSSION ON REFRACTORY MATERIALS.

Wednesday, November 8, 1916.

LIST OF EXHIBITORS.

SIR ROBERT HADFIELD.

DR. J. W. MELLOR, Stoke-on-Trent.

GEOLOGICAL SURVEY AND MUSEUM (Dr. A. Strahan and Mr. J. Allen Howe)—
Native Refractory Minerals.

IMPERIAL INSTITUTE (Professor W. R. Dunstan)—Colonial and Indian Refrac-
tory Minerals.

NATIONAL PHYSICAL LABORATORY (Dr. W. Rosenhain—Zirconia, and Mr.
Ezer Griffiths—Electric Furnace).

DR. R. LESSING—Illustrating Texture of Refractories.

THE EGLINTON SILICA BRICK COMPANY (Mr. W. Donald)—Magnesite and
Chrome Ore, Cement, Bricks, etc.

MESSRS. WILLIAMSON, CLIFF & CO., LTD., Stamford (Mr. Albert Cliff).

THE ROYAL WORCESTER PORCELAIN COMPANY, LTD.—Laboratory Ware and
Pyrometer Tubes.

MESSRS. J. W. KYLE & Co., Middlesbrough—Bauxite.

THE THERMAL SYNDICATE, LTD., Wallsend-on-Tyne—Silica Ware.

MESSRS. HADFIELDS, LTD., Sheffield.

MESSRS. ALLEN & SON, Halifax—Carborundum Fire Tubes, Muffle Clay.

MESSRS. AUGUST MUFFLES FURNACES COMPANY, LTD., Halifax—Carborundum
Fire Tubes, etc.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT COMPANY.—Pyrometers.

THE MORGAN CRUCIBLE COMPANY, LTD., Battersea.

THE A. Y. DINAS SILICA BRICK AND LIME COMPANY, LTD., Kidwelly.

MESSRS. GALLenkAMP, LTD.—Electric Furnaces.

MESSRS. HILL, WESTLAKE & Co., LTD., Cornwall—Firebricks.

MESSRS. STEPHENS & Co., Kidwelly—Silica Bricks.

MESSRS. B. GIBBONS, JUNR., LTD., Dudley.

MESSRS. TOWNSON & MERCER, LTD.—Alundum Refractories

MESSRS. J. H. SANKEY & SON, LTD., Canning Town.

MESSRS. E. J. & J. PEARSONS, LTD.

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Refractory Materials

(A GENERAL DISCUSSION held by the Faraday Society on Wednesday, November 8, 1916, SIR ROBERT HADFIELD, F.R.S., PRESIDENT, in the Chair)

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Reprinted from the *Transactions of the Faraday Society*,
Vol. XII, May, 1917.

The Faraday Society.

The Faraday Society was founded in 1903 to promote the study of Pure and Applied Electrochemistry, Electrometallurgy, Physical Chemistry, and Metallography.

The subscription to the Society is £2 a year for Members, and £1 a year for Students. Members also pay an Entrance Fee of £1, with the exception of Members of the Chemical Society, the Institute of Metals, the Institution of Electrical Engineers, the Iron and Steel Institute, the Physical Society, and the American Electrochemical Society, who are admitted **without Entrance Fee** and without the usual formal nomination.

The Society publishes quarterly or half-yearly *Transactions*, containing in full Papers which have been read with the discussions thereon, and reviews of books, and *Proceedings*, containing Reports and Notices of Meetings, with abstracts of the Papers read during the previous month and of the discussions thereon.

Under an arrangement between the Faraday Society and the American Electrochemical Society the **Transactions of the American Electrochemical Society** are sent without charge to all Members of the Faraday Society.

It is the practice of the Society to print all Papers before they are read at a meeting; advance proofs are sent to every Member, thus increasing greatly the value of the discussions, and giving absent Members an opportunity of expressing their views by correspondence.

One important feature of the work of the Society is the organization from time to time of a **General Discussion** on some subject of special interest. The Discussion is usually opened with a Paper summarizing the existing state of knowledge by some one exceptionally conversant with the subject, and every effort is made to secure representative opinions both by verbal contributions at the meeting and by correspondence.

Reprints of the following General Discussions can be obtained from the Secretary at the undermentioned prices :—

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